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Control of Mercury & Cadmium in Liquid Discharges

WS Atkins

R&D Project Record P4/028/1

Control of Mercury and Cadmium in Liquid Discharges

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Statement of use
The report reviews data on the sources of release of mercury and cadmium, and their compounds, to the environment. It identifies the most significant sources of these metals and estimates the quantities released and the trends in these data over recent years. The report will be of use, both internally and externally, to policy and operational staff in the development of methods to monitor and control the release of mercury, cadmium and their compounds to the environment.

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R&D Technical Report P105

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SUMMARY

This project record provides the detailed and supporting evidence used in the preparation of the R&D Technical Report titled "Control of Mercury and Cadmium in Liquid Discharges".

The Technical Report summarises our findings. Executive and Management Summaries together with limited discussions and our conclusions from the detailed investigation are presented. This R&D Project Record is the supporting detail of our investigations organised into 17 sections. Each section addresses a specific aspect or area of concern. Although extensive, the list of concerns is not exhaustive as there are other environmental problems becoming apparent, such as mine water pollution.

Together these reports conclude WS Atkins' assignment to research methods for the control of mercury and cadmium from industries regulated under the Environmental Protection Act and the Water Industries Act.

Its purposes are:

- to present the findings of a literature survey;
- to identify and where possible quantify UK sources and releases;
- to identify elimination, substitution or abatement techniques and the industries to which these are most applicable;
- to identify and investigate areas of future concern;
- to identify Best Available Techniques for controlling these releases including cost/benefit analysis.

We make it clear that this report is concerned with the discharge or release of mercury and cadmium (and their compounds) to the environment. The report makes no attempt to address the environmental harm or damage of these substances once released, nor does it address their influence on human health.

Accordingly we have met and communicated with a number of bodies representative of the mercury and cadmium industries, with other learned bodies, government experts and with providers of technology services. At the request of HMIP we did not hold discussions with mercury or cadmium processors until the broad issues were quantified and such encounters could be placed in their proper context by the regulators.

The original technical report was prepared between October 1993 and March 1994 for HMIP. Following the delay in publishing, it is necessary to refresh the 1994 report for publication in 1997. This revision includes new statistics and significant developments from the intervening years.

ACRONYMS & ABBREVIATIONS

BAT - Best Available Technique
BATNEEC - Best Available Technique(s) Not Entailing Excessive Cost
BPEO - Best Practicable Environmental Option
BS - British Standard
°C - Degrees Celsius
Cd - Cadmium and its compounds
CFL - Compact Fluorescent Lamp
CIGN - Chief Inspector's Guidance Note
DoE - Department of the Environment
DTI - Department of Trade and Industry
EU - European Union
EOP - End-of-pipe (technology)
EQO - Environmental Quality Objective
EPA - Environmental Protection Act 1990
ESP - Electrostatic Precipitator
FGD - Flue Gas Desulphurisation
g - gram
Hg - Mercury and its compounds
HMIP - Her Majesty's Inspectorate of Pollution
IPC - Integrated Pollution Control
IPCGN - Integrated Pollution Control Guidance Note
kg - kilogram (10^3 grams)
l - litre
m - metre
m^3 - cubic metre
MAFF - Ministry of Agriculture, Fisheries and Food
mg - milligram (10^{-3} grams)
ml - millilitre (10^{-3} litres)
mm - millimetres (10^{-3} metres)
ng - nanogram (10^{-9} grams)
NHS - National Health Service
NiCd - nickel-cadmium (cell)
NRA - National Rivers Authority
Red List - Substances identified for priority action in UK
SI - Statutory Instrument
te - metric tonne (10^6 grams or 0.984 UK tons)
μg - microgram (10^{-6} grams)
UK - United Kingdom
w/w - weight/weight basis
< - less than
> - more than

1. CONSUMPTION OF MERCURY & CADMIUM IN THE UK

In this section we present data on the mass movement of mercury and cadmium in the UK, either as mineral commodities or in domestic products. In line with other sources, we have defined the term 'consumption' in the following way:

CONSUMPTION: The mass of metal used by industry at the first processing stage. This does not account for subsequent recycling.

1.1 Import and Export Data

1.1.1 Import and export data are derived from UK Minerals Yearbooks 1992 and 1995 (British Geological Survey BGS) and Government sources (Central Statistical Office CSO) data for calendar years 1988 to 1995. Import and export information does not represent a definitive analysis of metal usage, as it does not account for home produced products used or recycled within the UK. It does, however, serve as an indication of the relative mass flux of mercury and cadmium to and from the UK. Mercury and cadmium masses present as trace contamination in raw materials such as bulk minerals are considered in Section 3.

1.2 Mercury Imports, Exports and Consumption

1.2.1 All virgin mercury metal is imported into the UK. Import and re-export of mercury during the last 5 years has been erratic as shown by Graph 1.1. Elemental mercury imports have decreased dramatically since 1988, whereas exports have increased in the same period. In 1995, some 4 tonnes were imported and 224 tonnes were re-exported.

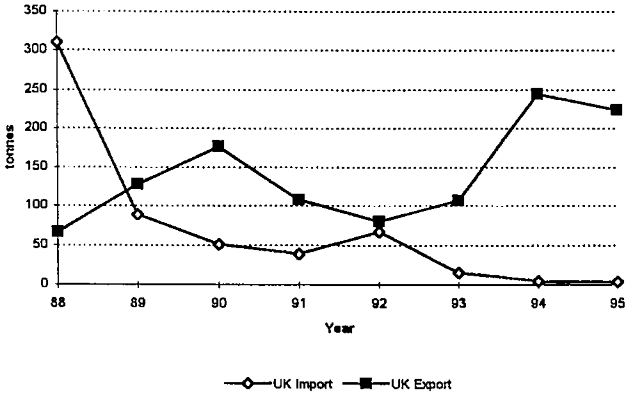
1.2.2 Elemental mercury is consumed directly, as in the chlor-alkali process or amalgam preparation, or converted to organic (mercurial) or inorganic compounds.

1.2.3 Elemental mercury is recovered from industrial and dental wastes by retorting. The extent of this secondary activity has not been assessed, but the production of recovered mercury must be significant.

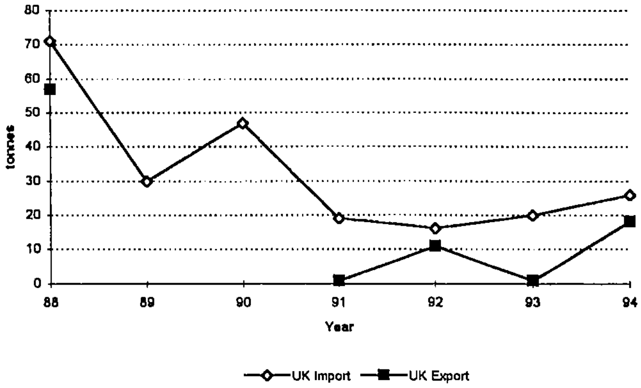
1.2.4 Other lesser elemental mercury uses include electrical equipment, such as mercury switches, and measuring equipment, such as thermometers. Triple distilled mercury metal is used to produce dental amalgams.

1.2.5 In addition to elemental mercury, mercuric oxide is also imported. Mercury oxide imports have decreased from 103 tonnes in 1987 to 26 tonnes in 1994 as shown in Graph 1.2, but there is a slight upwards trend. Exports of mercuric oxide have been low since 1991 although there was an increase in 1994. No organo-mercury imports or exports are listed for 1995 (BGS 1995). Mercury oxides are mainly used in primary button cells.

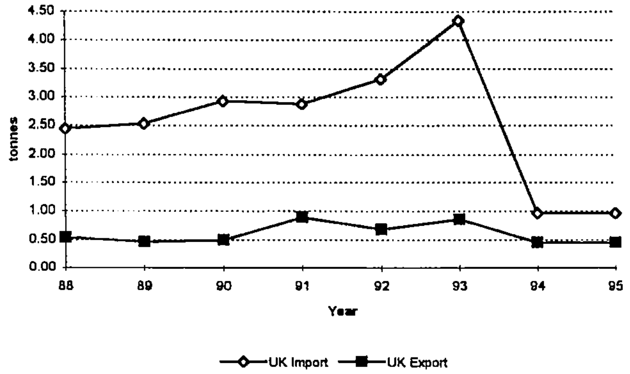
Graph 1.1 - Mercury Metal



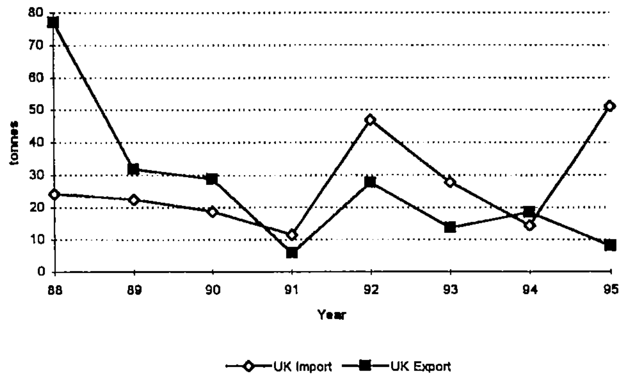
Graph 1.2 - Mercury Oxide



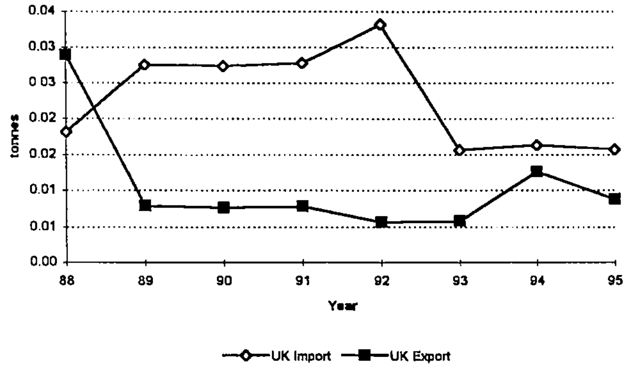
Graph 1.3 - Mercury in Alkaline Batteries
(@ 0.025% by mass)



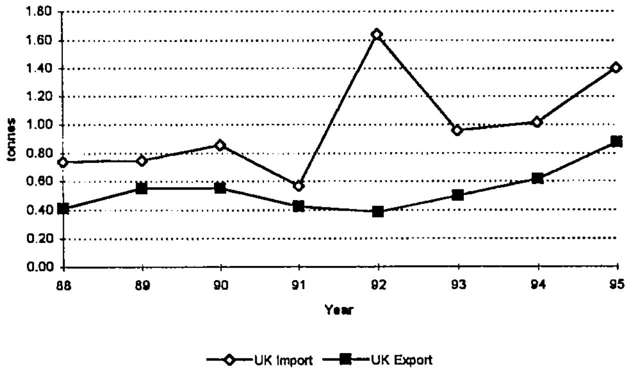
Graph 1.4 - Mercury in Mercuric Oxide Batteries
(@ 30% by mass)



Graph 1.5 - Mercury in Mercury Vapour Lamps
(@ 30mg / lamp)



Graph 1.6 - Mercury in Fluorescent Tubes
(@ 35mg / tube)



1.2.6 Mercury compounds are present in consumer products as an integral component. The major imports of mercury-containing products were portable batteries, such as alkaline manganese batteries, zinc-carbon cells or button cells. Mercury is also present in vapour lamps and fluorescent tubes.

1.2.7 An EU directive (91/157/EEC) prohibits the marketing of alkaline manganese batteries containing more than 0.025% by weight mercury (0.05% for those intended for use under extreme conditions). Other provisions of this directive require non-alkaline batteries containing more than 25 milligrams mercury to be subject to various economic sanctions, such as recovery, labelling and separate disposal. Regulations include for the marketing prohibition of certain batteries and the design of appliance requirements effective from 1 March 1994, and the obligation to label certain categories of battery with the EU symbol effective from 1 August 1994.

1.2.8 The proposed collection of certain categories of spent mercury-containing batteries is expected to apply to mercury and silver oxide button cells only as alkaline manganese and zinc chloride cells do not contain sufficient mercury to qualify.

1.2.9 The UK has no primary alkaline manganese battery manufacturing industry. Battery packs are fabricated here, but the majority of primary batteries are imported. The UK trend for the consumption of alkaline primary cells is increasing. In 1992 the net cell consumption was 10,510 tonnes increasing to 15,455 tonnes in 1995. However, mercury content in alkaline batteries has rapidly decreased after remaining consistently at around 0.025% w/w since 1988/89. This is because since 1994 all alkaline and zinc carbon batteries produced in the EU are mercury-free (European Portable Battery Association 1996) through a voluntary code of practice although imports from outside the EU may contain up to the permitted mass of mercury. In 1992, imports of alkaline batteries were equivalent to approximately 2.6 tonnes mercury per year at the nominal 0.025% w/w concentration; in 1995 this has decreased to approximately 1.0 tonnes as shown in Graph 1.3.

1.2.10 Button cells, commonly used in hearing aids and small electrical items, are exempted from the 91/157/EEC prohibition. A large proportion of button cells contain 30% by weight mercuric oxide as the cathode (CEST 1991), therefore button cells are alleged to contribute around 80% of the mercury sold in batteries even though they have less than a 3% market share. As alternative battery types are available now, mercuric oxide button cells are expected to decline in numbers to a minimum essential use with possible elimination by 1999 (European Portable Battery Association 1996). In 1992, the UK button cell net import was 64 tonnes of batteries equivalent to approximately 19.2 tonnes mercury (assuming all button cells were mercuric oxide). In 1995 the net import was 144 tonnes approximately equivalent to 43 tonnes mercury. In addition, we understand that button cells are manufactured in the UK. Graph 1.4 shows the erratic import pattern of this product which was the largest import of mercury to the UK in 1995.

1.2.11 The UK imports large quantities of lamps and fluorescent tubes which can contain up to 35 milligrams mercury per tube and 30 milligrams per lamp (DoE 1987). Graphs 1.5 and 1.6 show the relative flux of mercury contained in lamps and tubes. The mass of mercury imported in fluorescent tubes is increasing.

1.2.12 The total numbers of fluorescent tubes imported and exported in 1995 were approximately 40 million and 25 million respectively. For mercury lamps, the numbers imported and exported were 525 thousand and 292 thousand respectively. Overall this is equivalent to a net influx of less than 0.6 tonnes of mercury in 1995.

1.2.13 In past years, substantial mercury masses, over 9 tonnes in 1989/90 (OECD 1995), have been utilised in agrochemicals such as pesticides and fungicides. From March 1992, the sale, advertisement, supply, storage and use of products containing mercuric oxide, mercurous chloride and aryl and alkoxyalkyl mercury compounds ceased as the derogations applicable to directive 79/117/EEC have been revoked (Pesticides Safety Directorate).

1.2.14 Table 1.1 summarises information and estimates metal masses associated with the major end-uses of mercury, or mercury in finished products, in the UK since 1973. We also suggest the likely trend in the uses according to recent legislation implementation.

1.2.15 The import / export figures show that the UK's exports of mercury consistently outweigh imports for the last three years, implying that the UK is either reducing its inventory of mercury or has an unrecognised production capacity. Historically, countries such as the US and former USSR have stockpiled mercury for defence related purposes, which is now being released onto the metal trading market. It is not known if this is the situation in the UK, although it is known that the chlor-alkali industry has stockpiled mercury in the past.

Table 1.1 - Mercury Metal Consumption in the UK

Application	1973[1] Tonnes	1975[2] Tonnes	1989/90[3] Tonnes	1992[4] Tonnes	1995[4] Tonnes	POST 1995 - Trend Estimate
Chlor-alkali industry	221	283	52	<45	<40	Will DECREASE as replacement membrane plants commissioned; little change in short term
Primary batteries (button cells)	80	80	16.1	16	<20	Will DECREASE as industry moves to mercury-free alternatives
Paint production	35	34	?	<1	<1	NEGLIGIBLE baseline level for export
Dentistry	30	30	11.4	17	8.1	Will DECREASE as less amalgam used.
Agriculture and related uses	27	28	9	<1	<1	DECREASE, mercury in pesticides & agrochemicals banned in 1992. Some production for export expected.
Electrical equipment and control instruments	14	14	?	2	2	NO CHANGE, baseline use in lamps & tubes essential May increase slightly with widespread CFL use.
Catalytic	11	11	?	?	?	May DECREASE due to IPC
Laboratories use	10	10	?	<1	<1	DECREASE to NEGLIGIBLE as large laboratories routinely use mercury free reagents
Pharmaceutical industry	2	2	?	<1	<1	Baseline level NO CHANGE as health related use
Other identified uses	6	7	?	<1	<1	DECREASE on basis of increasing awareness and IPC
Total	436	499	89.5	<85	<75	Will DECREASE significantly when Chlor-alkali industry changes to new technology and button cell production reduces.

Sources : 1 - Pollution Paper No 10 (DoE 1976); 2 - Waste Management Paper No 12 (DoE 1977); 3 - OECD Report 1995; 4 - WS Atkins estimate

1.2.16 Therefore the categories of mercury use effectively reduced now or likely to be eliminated are;

- chlor-alkali produced caustic soda;
- alkaline batteries and zinc-carbon cells;
- paints;
- agricultural chemicals such as pesticides, biocides and seed dressings;
- laboratories where the large scale use of mercury catalysed reactions such as the COD determination are now carried out using mercury free reagents.

The battery industry expects mercury oxide button cells to be replaced by mercury free or low mercury batteries, although there is no indication of this yet.

1.2.17 Alternatives to mercury use in electrical rectifiers and in measuring instruments such as thermometers will reduce the flow of mercury metal into these products although the existing mercury inventory in these items will decrease only with breakage and wastage, i.e. mobilisation.

1.2.18 Therefore the significant end-uses of mercury remaining in the longer term (excluding the chlor-alkali industry) are;

- dental amalgam;
- electrical equipment including fluorescent tubes and vapour lamps;
- possibly mercury catalysts.

1.2.19 Although the sale or use of the mercury-containing compounds may no longer take place in the UK, manufacturing capacity for export purposes may still exist for such materials as mercurial for agricultural use overseas or pharmaceutical use. Increasing pressures may drive this manufacturing capacity overseas to the areas where use is still tolerated.

The current primary consumption and release of mercury remains the chlor-alkali industry. However, this industry is committed to replacing the mercury cells with mercury free processes thereby making today's other secondary consumptions important for future control. The elimination or reduction of mercury use in most batteries, paints, agricultural chemicals and laboratories leaves electrical appliances as intractable essential uses. Dentistry remains as an area where significant reductions are feasible.

1.3 Cadmium Imports, Exports and Consumption

1.3.1 Cadmium is produced in the UK as an inevitable by-product of zinc smelting. About 95% of the world production of primary cadmium arises as a by-product from the primary production of zinc, the rest is made up from lead and copper smelting. Zinc production in the UK has risen by some 25% since 1988 to around 100,000 tonnes per annum.

1.3.2 Therefore UK cadmium production is steadily increasing, as shown in Graph 1.7, from 399 tonnes in 1988 to 549 tonnes in 1995 (World Bureau of Metal Statistics 1996).

1.3.3 Conversely Graph 1.7 shows UK cadmium consumption declining steadily since 1988. UK production and consumption are converging such that the UK may become a net cadmium metal producer in 1996. This is confirmed by cadmium metal exports exceeding imports for the first time in 1995 as shown in Graph 1.8.

This may cause excess cadmium disposal to be an issue if the market for this material is diminishing in the UK.

1.3.4 The UK is a net exporter of cadmium pigments, as can be seen in Graph 1.9. Exports of cadmium pigment have declined to less than 50% of the 1988 total.

1.3.5 Cadmium is imported in end-products, particularly nickel-cadmium (NiCd) accumulators for domestic consumption, but also as trace levels of stabilisers or pigments in finished products such as plastics, particularly PVC products.

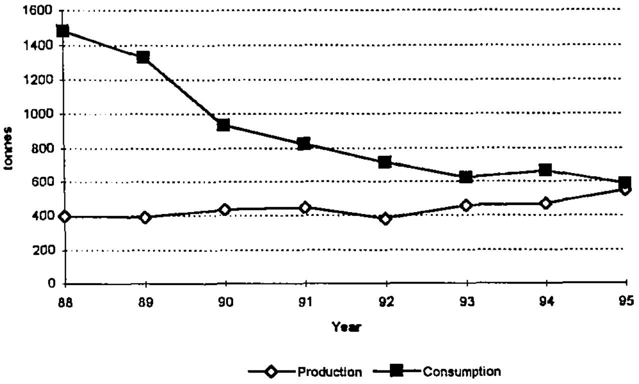
1.3.6 NiCd accumulators represent the largest single import of cadmium in end-products. The cadmium content of NiCd cells ranges from 18 to 22% w/w (OECD 1995). Imports of these cells continues to increase to facilitate more use of rechargeable portable appliances.

1.3.7 We understand that the UK does not manufacture small NiCd accumulators, although it is possible that industrial cells are produced in the UK. The flux presented is further distorted by NiCd cells being imported, incorporated into products and then re-exported. Graph 1.10 shows the flux for NiCd accumulators. In 1992 some 35.8 million sealed cells were imported and 2.5 million cells exported. On the basis of a 20% cadmium content, the net UK cadmium influx was approximately 485 tonnes in 1992. In 1995 this had increased to 520 tonnes.

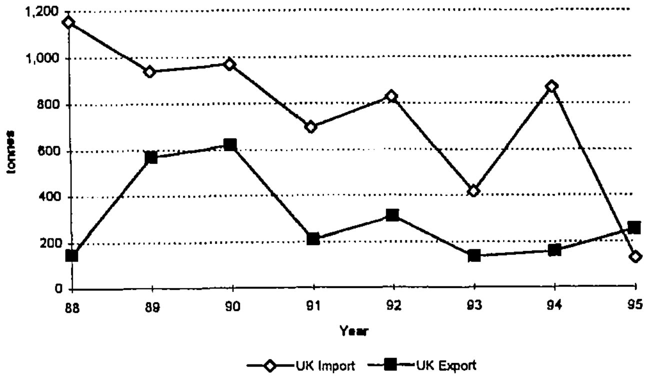
1.3.8 Commercial cadmium recovery from scrap metal is thought to be minimal on account of the low market price for the metal. Cadmium is volatilised by most pyrometallurgical operations and concentrates in the particle fraction removed from the flue gas stream.

1.3.9 The principal uses of cadmium metal and compounds in the UK are summarised in Table 1.2 together with an assessment of short term industrial trends.

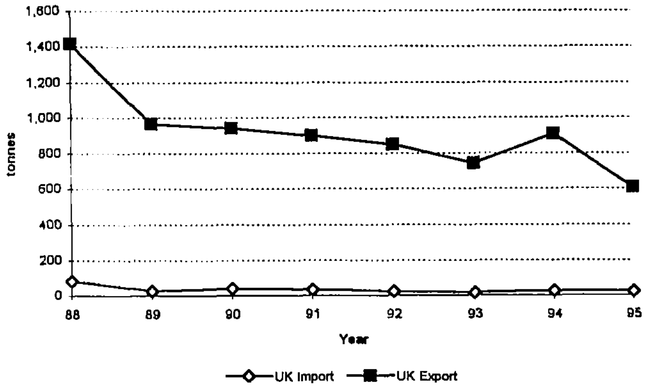
Graph 1.7 - Production and Consumption of Cadmium in the UK



Graph 1.8 - Cadmium Metal



Graph 1.9 - Cadmium in Pigments



Graph 1.10 - Cadmium in NiCd Sealed Batteries (@ 20% by mass)

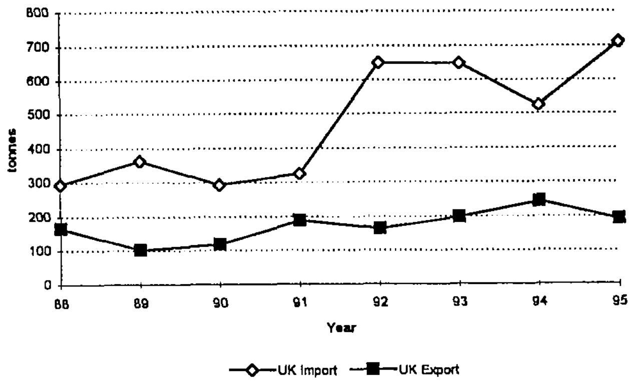


Table 1.2 - Cadmium Consumption in the UK

Source	1978[1] Tonnes	1984[2] Tonnes	1992[3] Tonnes	1995[4] Tonnes	POST 1995 > Trend Estimate
Pigments	550	630	356	310	Limited DECREASE in production and consumption expected post 1995 as most production exported
Stabilisers	100	158	Included in miscellaneous	Included in miscellaneous	DECREASE in production and consumption expected post 1995 as SI 1993 1643 restricts use to essential safety related applications only.
Surface Coatings especially electroplating Including anodes and salts	430	323	147	80	Baseline level to supply safety and defence related applications as described by SI 1993 1643. Industry consists of fewer,but larger companies in response to IPC authorization.
Alloys	70			70	Minor uses, expected to show slow DECREASE
Cd - Cu			3		
Solder			25		
Others			12		
Miscellaneous including Electrical, Semiconductors	40		171	100	Semiconductor manufacture likely to INCREASE, but only represents a small mass of cadmium. Other uses expected to DECREASE as per SI 1993 1643.
Total Consumption[3]	1,190	1,283	715	558	Consumption expected to DECREASE slowly in all sectors except battery manufacture which could cause a net INCREASE in consumption if UK restarts battery manufacture in response to market forces.

Sources : 1 - Pollution Paper No 17 (DoE 1980); 2 - Waste Management Paper No 24 (DoE 1984); 3 - World Bureau of Metal Statistics (1996); 4 - WS Atkins estimate

1.3.10 UK regulation implemented in response to EU directives restricts cadmium uses across a wide spectrum of products. This market restriction will reduce cadmium releases from industry in turn. SI 1643 came into force in July 1993 implementing EU directive 91/338/EEC restricting cadmium uses to those principally associated with essential, safety related applications. SI 1643 addresses cadmium use in, content and marketing of finished products and components associated with colouring, stabilisers and surface coating.

1.3.11 SI 1643 prohibits the use of cadmium colours in a variety of plastics and some paints, and also prohibits the marketing of such finished materials or components coloured by cadmium. Marketing of some plastics with an inherent cadmium content is permitted only when the cadmium content does not exceed 0.01% by mass. Certain paints with a high zinc content can only be placed on the market if the residual cadmium content is as low as possible and does not exceed 0.1% by mass. The prohibitions were effective from 31 July 1993 and 31 December 1995.

1.3.12 In 1992, the UK used some 357 tonnes of cadmium in pigments (Cadmium Association 1992). Some 898 tonnes of pigment were exported in 1992 suggesting UK pigment production capacity was in excess of 1,250 tonnes per year. In 1995, 606 tonnes of pigment were exported mainly to countries outside the EU. The 1995 UK pigment consumption has been estimated as 310 tonnes in the absence of data.

1.3.13 SI 1643 also prohibits the use of cadmium stabilisers in various finished products and the placing of such materials on the market, effective from June 1994. Also, marketing of such materials is prohibited if the cadmium content exceeds 0.01% by mass of polymer.

1.3.14 Cadmium plating and marketing of cadmium plated products is also addressed by SI 1643. Effective from 31 July 1993, cadmium plating of equipment or components used for various production categories, including food production and agriculture, is prohibited as well as the placing on the market of such materials.

1.3.15 Consumption of cadmium by electroplating has decreased steadily in response to the increasing legislative pressure, consumer awareness and the availability of alternative metal surface coating treatments.

1.3.16 In the UK, we estimate there are around 15 electroplaters consuming some 80 tonnes of cadmium in 1995. This represents nearly a 46% decrease on the 1992 quantity of 147 tonnes (Cadmium Association 1992). The cost of meeting IPC obligations is prohibitive to small plating companies, therefore the cadmium plating industry has contracted until only a small number of large companies remain supplying the market demand for cadmium plating business.

1.3.17 No common coating technique can replace all the properties associated with cadmium coatings, particularly electrical resistance and lubricity. However, zinc/nickel deposits offer equivalent performance in non-electrical applications and other finishes have superior corrosion resistance.

1.3.18 The measures included in SI 1643 specifically do not apply to the use of cadmium for research and development, or the use of cadmium in finished products coloured or stabilised with cadmium for safety reasons. SI 1643 does not apply to cadmium plating of products or components requiring high safety standards such as may be used in aeronautical, offshore, mining, aerospace and safety devices in various vehicles, and also electrical contacts where reliability is required.

1.3.19 The definition of "essential" safety applications by whom and how this legislation will be policed is not clear at present. Many of the existing uses of cadmium are within safety related areas, for example the principle of using cadmium based stabilisers for disposable plastic medical products is indicative of areas where elimination of cadmium may be questioned on an "essential" basis. Until further guidance is available on which uses are exempted by the legislation, it is impossible to provide a quantitative forward projection for cadmium use in the year 2000 until these questions are resolved.

1.3.20 We expect cadmium pigment and stabiliser use will decrease as alternative materials are currently available, although performance may be less compared to the cadmium based treatment. However, the use of cadmium colours and stabilisers in safety applications is well established and is unlikely to decrease significantly in the short term.

1.3.21 We do not expect that SI 1643 will reduce the mass of cadmium plated significantly on the basis that contraction to baseline business has already largely occurred in the industry and most of the current applications will be justified on safety related grounds. However, the price for cadmium plating is likely to rise due to the obligatory IPC capital and operational overheads. This may make coating alternatives more economically viable.

1.3.22 Overall the UK consumption of cadmium metal has declined steadily in the last six years as a result of environmental pressures and legislation. New legislation restricting the use of cadmium in non-essential applications will reduce cadmium metal and compounds consumption further in the UK.

1.3.23 The increased use of cadmium in products, particularly rechargeable batteries, has offset the reduced cadmium use in other areas. Increased battery numbers and sizes, especially as traction batteries in electric vehicles, could cause a short term increase in cadmium consumption worldwide. This will be reflected in an increased UK import of these cadmium containing products.

1.3.24 The UK pigment and stabiliser industries will contract to an unknown extent depending to a large extent on overseas markets.

1.3.25 Cadmium electroplating has decreased to near a baseline capacity to service the "essential" use components market. Cadmium use in semiconductors and photovoltaic applications is likely to increase, but this is currently only a minor use due to the thin film technology utilised.

1.4 Other Sources

1.4.1 Mercury and cadmium are present as trace contaminants in other minerals imported by the UK. Important bulk materials in this context are coal and oil. Phosphate rock used to be imported for phosphoric acid production, however, this practice has now stopped although imported phosphoric acid may still contain cadmium depending on the source.

1.4.2 Cadmium is present as a naturally occurring contaminant in non-ferrous plating solutions and anodes, particularly zinc and to a lesser extent electroless nickel and gold solutions. Approximately 3,500 tonnes of zinc are plated annually and if the maximum zinc anode cadmium content is 0.0005% then approximately 17.5 kg cadmium are released from this activity resulting in higher than background levels.

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2. SOURCES AND RELEASES

2.1 Releases

2.1.1 In this section we review information from diverse sources to formulate an appreciation of current UK sources and releases of mercury and cadmium (and their compounds) to the hydrosphere. This includes addressing mercury and cadmium releases from industry as well as the broader aspects of mercury and cadmium release to coastal waters.

2.1.2 In addition to mercury and cadmium emissions from natural sources, the metals are released to environmental compartments;

- directly from industrial processes as waste or effluent;
- in end-products from domestic consumption e.g. batteries;
- in the population's waste e.g. sewage, amalgam filling leaching;
- from bulk commodities containing trace contaminations, such as minerals or municipal solid waste.

For the purposes of this study, natural releases are not considered further unless relevant, although natural sources will influence metal burden estimations to the North Sea.

2.1.3 The UK, together with the EU, Nordic countries and America, is in a transient phase regarding release of mercury and cadmium to the environment. Significant decreases in mercury and cadmium use and release from most sources have occurred, mostly within the last five years.

2.1.4 The magnitude and speed of the reductions occurring have resulted in little or no recent environmental overviews of the UK situation. Published work tends to be reliant on studies performed prior to 1986 although a broad ranging study for the UK was recently published (DoE 1996) for mercury.

2.1.5 Since 1983, the industrial process capacity and product range in the UK has changed, IPC has been introduced, consent to discharge trade effluent limits and air emissions limits have become more stringent and therefore the composition of waste materials has altered with respect to the mercury and cadmium content.

2.1.6 The sources and release information presented in this section is indicative of the overall situation only and applies to the year given. Information is extrapolated to 1995 where possible. Also where possible, mercury and cadmium load data have been qualified to reflect the current situation. We have presented simple matrices to show potential for releases from point sources in 1995.

2.2 Mercury - Published Work

2.2.1 An UK overview was published (Hutton et al. 1986) on mercury emissions to various compartments based on emission factors and observed data for circa 1984.

2.2.2 This overview concluded that for the period encompassing 1980 to 1984, overall annual mercury emissions to the atmosphere and landfill were 51 and 113 tonnes respectively. 7.1 tonnes per year were disposed in sewage sludge and 38 tonnes reached coastal waters of which 9.5 tonnes were derived from industrial discharges, 14 tonnes from rivers and 11.2 tonnes from dredged materials. The other data from this study are summarised in Table 2.1.

2.2.3 Supplementary notes to this work included comments that 52 tonnes of mercury per year could not be accounted for in any of the waste streams from the chlor-alkali industry. The fate of mercurials is not given, but would have included use in paints and pharmaceuticals. Table 2.1 emphasises the contribution of the chlor-alkali industry to environmental releases, the large proportion of mercury entering landfills and the quantity of mercury associated with trace contaminations in fossil fuel and municipal solids waste.

2.2.4 In the absence of a recent mercury release overview for the UK, we have presented, in Table 2.2, a summary review cited in the OECD report (OECD 1993/1995) which reviewed immediate mercury releases throughout the EU in 1989. This review estimated the destination of immediate mercury emissions in the EU by industrial sector expressed in tonnes per year. The exact criteria used for this table were not given, however some notable categories are not directly identified including waste combustion or energy generation, agricultural chemicals and pharmaceuticals.

2.2.5 As the UK was not identified separately in this overview, we have assumed the mercury use pattern in the UK is similar to that of the overall EU with respect to percentage contributions to environmental compartments. Overall, the OECD summary concluded 26% of the total EU mercury emission to all compartments was discharged to atmosphere, 5% to water and 69% to land. This summary proportioning is similar to the 1986 UK overview (Hutton et al) that estimated approximately 65% of mercury release was to land, 27% to atmosphere and 8% to water in 1983.

Table 2.1 - UK Mercury Emissions to Various Environmental Compartments for 1983

Use	Consumption tonnes	Atmospheric Emission tonnes	Landfill Disposal tonnes	Municipal Waste tonnes	Arable Land Disposal tonnes	Water Emission tonnes	Recycle tonnes
Chlor-alkali industry	211	9.7	40.6	0	0	8	10.1
Mercurials	160	0	ND	0	0	0	0
Batteries	95-110	<0.1	2	42 -53	0	0	18 - 21
Catalysts	28	0.4	3.9	0	0	ND	21.9
Dentistry	21	ND	ND	ND	0	6	11.5
Pesticides	12	0	ND	0	12	0	0
Fossil fuel combustion	-	25.5	1.8	-	-	-	-
Ferrous metal industry	-	1.8	-	-	-	-	-
Non-ferrous industry	-	5.0	ND	-	-	ND	-
Solid wast	-	-	-	62	-	-	-
Sewage sludge disposal	-	5.9	1.7	-	1	-	-
MSW incineration	-	5.9	0.7	-	-	-	-
Cement production	-	2.5	-	-	-	-	-

Source - Hutton and Symon 1986 ND - No data available

Table 2.2 - Mercury Emissions in the EU in 1989

Source/Activity	To Air tonnes/year	To Water tonnes/year	To Land tonnes/year	Total tonnes/year
Mercury Mining	10	?	20	30
Secondary Production	5	<1	15	21
Non Ferrous Metal Production/Refining				
- Zinc - cadmium	4	<1	16	20
- Lead	1	<1	2	3
- Copper	1	<1	1	2
SUB TOTAL NON FERROUS	6	1	19	26
Fossil Fuels				
- Coal	48	<1	12	60
- Oil	24	-	-	-
- Natural gas	4	-	-	-
SUB TOTAL FOSSIL FUELS	76	<1	12	88
Industrial Production				
- Iron/steel	4	2	28	34
- Chlorine/caustic	23	5	150	178
- Industrial catalysts	?	<1	?	<1
- Cement	2	-	26	28
- Fertiliser	<1	1	3	4
SUB TOTAL INDUSTRIAL	29	8	207	244
Product Use				
- Batteries	33	<1	100	133
- Dental amalgam	8	14	24	46
- Electrical lighting and	10	<1	30	40
equipment	6	<1	19	25
- Measuring instrumentation	1	1	6	8
- Laboratory application	-	-	11	11
- Fertilizer	4	<1	12	16
- Industrial catalysts				
SUB TOTAL PRODUCT USE	63	17	202	282
Sludge Disposal	3	2	28	33
Cremation/burial	4	-	6	10
Dredging	<1	6	20	26
Totals	**197**	**35**	**529**	**761**

Source - Maxson et al cited by OECD 1993 and 1995

2.2.6 The salient points from these overviews regarding mercury are;

- fossil fuel combustion is identified as the single largest contribution to atmosphere; the releases from coal combustion are well established, but the situation regarding contamination in oil and gas extraction and refining are not identified;
- dentistry and the chlor-alkali industry are the largest mercury contributions to water;
- residues from the chlor-alkali industry are the biggest contribution to landfill, followed by batteries and then approximately equivalent contributions from most industrial sectors;
- hitherto minor industrial emissions such as from cement production and non-ferrous metal processing will become more significant when the mercury cell chlor-alkali industry contribution is gone;
- the majority of mercury emissions are to landfill and atmosphere; only a small percentage of the total is discharged to water;
- dredging is a significant emission to water;
- mercury in products results in releases to all media.

2.3 Cadmium - Published Work

2.3.1 A UK overview on cadmium release was published (Hutton et al. 1987) regarding point sources in 1983. Total cadmium releases were estimated as 14 tonnes to atmosphere, 43 tonnes to agricultural land, 880 tonnes to landfill, 3 tonnes to freshwater and 42 tonnes to estuarine and coastal waters.

2.3.2 Four main uses were identified for cadmium and cadmium compounds; pigments, electroplating, NiCd batteries and stabilisers. This analysis is summarised in Table 2.3. This work recognised that a substantial portion of the cadmium consumption entered the environment in end-products that would ultimately reach the waste disposal pathway.

2.3.3 Cadmium releases to water were estimated at 2.0%, 1.3% and 5.0% of the consumption for pigments, stabilisers and electroplating respectively. With IPC, these releases will be substantially lower in 1996.

2.3.4 Cadmium release is associated particularly with zinc smelting. Currently there is only one UK primary zinc production facility located at Avonmouth. Zinc production produces a waste (jarosite deposit) that represents a high volume, low cadmium concentration waste in which the cadmium is relatively immobile. This material is either stockpiled or deposited in landfill where it represents a potential cadmium leaching source. The quantity of cadmium in non-ferrous industry slag is estimated as 20 tonnes per year (Hutton et al. 1986).

2.3.5 By 1992, the cumulative quantity of cadmium consumed by the UK pigment, stabiliser and electroplating industries had substantially reduced compared to 1983. Likewise the proportion of cadmium consumed entering aqueous waste has been reduced by IPC regulation.

2.3.6 There are currently two pigment manufacturers and two stabiliser manufacturers in the UK (see Section 5).

2.3.7 At the start of 1993 there were approximately 40 UK companies offering cadmium plating services; this number is thought to have reduced to around 15 at the end of 1995 (Personal communication Metal Finishing Association).. The cadmium mass consumed (i.e. plated or released) has reduced to around 80 tonnes in 1995/96 with the market dominated by fewer, but larger, companies that can bear the financial burden of IPC.

2.3.8 Cadmium is used in alloys to impart special properties to other metals. Examples of this application include adding cadmium to copper to impart increased strength and conductivity, to improve solder properties, or in corrosion protection to ensure an even corrosion rate.

Table 2.3 - Cadmium Releases in UK 1983

Source/Activity	**Cadmium Consumption tonnes**	**Air tonnes**	**Water tonnes**	**Landfill tonnes**	**Waste Pathway tonnes**
Cadmium Industry					
- Pigments	630	?	13	13	606
- Stabilisers	158	?	2	2	154
- Semi conductors	?	?	?	?	?
- NiCd batteries	200	?	3	-	57
- Electro Plating	323	?	16	191	116
SUB TOTAL INDUSTRY		?	34	206	
Fossil Fuels					
- Coal		2.2		105.5	78.5
- Oil		0.02			
- Natural gas		?			
SUB TOTAL FOSSIL FUELS		2.2	?	105.5	78.5
Municipal Waste Disposal					
- Landfill		-	-	450	
- Municipal Waste Incineration		4.5		41	
- Medical Waste Incineration		?		?	
SUB TOTAL MUNICIPAL WASTE DISPOSAL		4.5		490	?
Non Ferrous Metals				20	
- Zinc (cadmium) smelting		3.7	2.6	0.8	
SUB TOTAL NON FERROUS METALS		3.7	2.6	21	
Ferrous Metals Production					
- Iron		1.0	0.2	8.1	
- Steel		1.5	1.5	32.5	6.8
SUB TOTAL FERROUS METALS		2.5	1.7	40.6	6.8
Cement Production		1.0	-		21
Fertilizer		-	5.7		1.3
Sewage Sludge					
- to land		-	?		7.5
- incineration		0.2	?		?

Source - Hutton and Symon 1987
? - No data

2.3.9 Cadmium is being increasingly used in photovoltaic semiconductor materials usually combined with tellurium, selenium or as cadmium sulphide (Personal communication Cadmium Association). Although this is a growth area, the quantities of cadmium concerned are small due to the thin film technology employed. Nevertheless there is potential for above background level cadmium releases and the export of cadmium in finished products ultimately entering the waste pathway.

2.3.10 A more recent guide to locating and estimating air emissions from sources of cadmium and cadmium compounds in the EU was published (OECD 1995), but no UK data was given.

2.3.11 Table 2.3 clearly shows that the majority of cadmium releases are associated with trace contamination in raw materials or waste products. Industries producing cadmium containing products are dissipating the metal into the environment as a diffuse source. A prime example of this is NiCd battery manufacture and use leading to entry into the waste pathways. Cadmium release at the point of manufacture is controlled, but the end point use and disposal is not.

2.4 Other Environmental Release Studies

2.4.1 In 1989 an inventory of aqueous point sources of Red List Substances in England and Wales by questionnaire was carried out (Water Research Centre 1990). 14,700 questionnaires were issued to potential dischargers and received 6,500 replies. Although WRc found the results of the survey suspect, some of their conclusions are of interest. They found;

- the most common red list substances released were cadmium (34%) and mercury (18%);
- that 428 cadmium and 225 mercury releases were declared. Some 650 companies used cadmium material although only 428 released it;
- trace concentrations of mercury and cadmium were present in effluent without companies' knowledge, or were not declared in the questionnaires.

2.4.2 WRC classified their findings in terms of major and trace releases on an industry by industry basis as shown in Table 2.4.

Table 2.4 Major and Trace Releases by UK Industry 1989

Industry Category	Cadmium			Mercury		
	No. of releases			No. of releases		
	Trace	Major	% of releases	Trace	Major	% of releases
Food & Drink manufacture	-	-	-	20	-	9
Engineering	166	1	39	16	-	7
Industrial chemical manufacture	27	1	7	46	1	21
Other non-chemical manufacture	72	1	17	18	-	8
Vehicle/aerospace manufacture	32	-	7	-	-	-
Research				26	-	12
Miscellaneous industries	88	-	21	71	1	31
Medical Institutions	-	-	-	26	-	12
Unknown/unspecified	39	1	9	-	-	-
Total	424	4	100	223	2	100

2.4.3 For mercury, two major releases (not named) were identified in the UK and the majority of identified trace releases were attributed to the chemical industry. Trace releases were spread over a diverse range of industrial activities, with research and medical activities being substantial fractions. Anecdotal evidence suggests some of these are due to mercury contamination of technical grade caustic soda.

2.4.4 For cadmium, engineering was identified as the major process release (presumably including electroplating). Other manufacturing and diverse applications contributed substantial numbers of trace releases. Four major point source cadmium releases were identified.

2.4.5 WRc included further survey data on trace releases; out of 87 companies returning questionnaires, 29 contained mercury over 0.1 μg/l and 21 contained cadmium in excess of 5 μg/l. Mercury was detected (detection limit 0.008 μg/l) in effluent from 71 companies and cadmium in 74. 24 companies reported releasing mercury, although for 9 of these no mercury was detected, and 20 companies reported releasing cadmium although no cadmium was detected in 7 of these.

2.4.6 This 1989 study indicated that trace aqueous releases of mercury and cadmium were relatively common and may have been occurring in ignorance of the companies involved. Hitherto obscure processes and activities using mercury and cadmium materials could give rise to metal concentrations above background levels in liquid discharges.

2.4.7 In 1996 IPC has addressed this by including guidance on trace contamination in raw materials such as caustic soda in IPC Guidance Notes.

2.4.8 Trace water contamination from activities involving cadmium containing items, particularly safety related applications, such as aircraft maintenance where cadmium plated components are removed and cleaned, were considered for IPC. However, the 1994 threshold mass IPC exemption amendment (1,000 and 200 grams in a 12 month period for cadmium and mercury respectively) to the Environmental Protection (Prescribed Processes and Substances) Regulations means such discharges are regulated by the sewerage undertaker only.

2.4.9 An overview report (WRC 1986) summarised the heavy metal releases in the UK. This report considered inputs to the environment from various sources. A summary of assessment of inputs to environmental compartments from their work dated circa 1983 is given in Table 2.5.

Table 2.5 Mercury and Cadmium Release to Environment 1983

Environmental Compartment	Cadmium % contribution to compartment	Mercury % contribution to compartment
Atmosphere	2	21
Farmland	6	14
Landfill	83	50
Other land	<1	<1
Rivers	<1	2
Coastal Waters	8	13
Total	100	100
Total load tonnes	754	214

2.4.10 This overview concluded over 80% of emissions ultimately reached landfill and only small proportions entered the sewerage system. Other information in this report estimated runoff from roads to be 3.7 tonnes per year and 0.1 tonnes per year for cadmium and mercury respectively. The mercury and cadmium contribution to rivers was thought to be 2% of the total or less.

2.4.11 In this overview the mass balances and metal pathways for mercury suggested that most of the mercury releases are accounted for, but this was not the case for cadmium. As others have found before, industrial releases via the sewerage system do not account for the riverine cadmium load. Other workers have attributed this to diffuse sources which could include natural sources, drainage from mines, spoil heaps or deposition.

2.4.12 Since 1983 the mass of mercury and cadmium discharged by industry has reduced and the percentage of the metals reaching landfill has increased due to improved capture and the elimination of metals from many trace sources.

2.4.13 Our conclusion is that the river metal load surveys show the success of point source regulation and that further reductions in riverine mercury and cadmium loads may be difficult to achieve if industrial point sources are already effectively eliminated and diffuse sources contribute a high proportion of the load.

2.5 Controlled Waters Survey - England and Wales

2.5.1 A 1994 survey (NRA 1995) quantified pollutant releases to coastal waters for England and Wales including data on cadmium and mercury. For each parameter, the sources of these emissions were summarily classified as "Industrial", "Rivers" and "Sewage". The classification reference point was the river sampling location located just above the tidal limit. All discharges above this point were classified as river, all discharges below were identified as either industrial or sewage representing direct coastal discharges.

2.5.2 Although this data does not resolve contributions from inland natural, industrial or sewage sources, it does compare the total annual inputs from direct discharges into estuaries and coastal waters with that from inland sources in 1994 as shown in Table 2.6.

The two estimates given represent concentration data below the limit of detection as either zero (low estimate), or high (at lowest limit of analytical detection).

Table 2.6 - Cadmium and Mercury Releases to Coastal Waters around England and Wales 1994

Substance	Input tonnes	Industrial %	River %	Sewage %
Cadmium				
(low)	10.9	41.99	52.50	5.12
(high)	17.7	27.16	66.36	5.37
Mercury				
(low)	1.7	37.55	57.05	4.68
(high)	3.8	17.28	77.31	4.34

low = zero load

high = limit of detection load (see text)

Source NRA 1995

2.5.3 Table 2.6 clearly confirms that most of the mercury and cadmium load reaching coastal waters is discharged above the tidal limit of the rivers although direct industrial discharges represent a significant input.

2.5.4 The NRA presented their survey data on a zonal basis, according to 30 coastal zones, as defined by the International Council for the Exploration of the Sea (ICES). Quantities were given for mercury and cadmium loads which were attributed to the three categories of source.

2.5.5 For mercury, the survey found that in 1994 the four biggest contributors were the Mersey Estuary (19.57%), the Humber Estuary (18.46%), the Northumbrian coast (11.15%) and The Wash (10.47%). The main source was identified as industrial for the Mersey Estuary, but the other three included a substantial natural contribution. Mercury contributions from other zones were consistently low. River loads exceeded industrial and sewage loads in almost all cases.

2.5.6 The single largest cadmium load was discharged on the Cumbrian coast from a single industrial phosphatic rock processing source. The second and third highest cadmium loads were discharged to the Severn Estuary and eastern South Wales coast respectively. Industrial cadmium discharges dominated the Cumbrian coast, Tees Estuary, North Yorkshire coast and Severn Estuary discharges, but sewage and river loads dominated the remainder.

2.5.7 Cadmium discharges were consistently low except for three zones, which together contributed 39% of releases. In all, but 6 of the 30 zones, rivers contributed the majority of cadmium releases. Of these zones, industrial sources contributed the majority in four cases, with sewage being the majority source in the remaining two.

2.5.8 The 1994 survey data for England and Wales (NRA 1995) in conjunction with High Load data from 1990 and 1991 indicates the downward trend in the release of cadmium and mercury to coastal waters. This is summarised in Table 2.7.

Table 2.7 - Trends in Mercury and Cadmium Load to Coastal Waters around England & Wales (High Load Data)

Source	1990	1991	1994
Cadmium			
Total Input (tonnes)	46.0	34.5	17.7
% Industrial	53	27	27
% River	30	48	66
% Sewage	17	25	5
Mercury			
Total Input (tonnes)	9.1	6.5	3.8
% Industrial	35	38	17
% River	58	61	77
% Sewage	4	4	4

(adapted from NRA data)

2.5.9 Overall the total mass input of cadmium displays a downward trend, with the proportion from industrial sources appearing to stabilise at around 27%. The contribution from coastal sewage discharge has fallen whereas the residual proportion from riverine (inland) sources has risen.

2.5.10 The total input of mercury has also fallen in mass terms. Overall the industrial proportion has reduced, the proportion from sewage appears to have stabilised, and that from rivers has increased.

2.5.11 In 1994, the input of mercury and cadmium to coastal waters around England and Wales represented 52.1% and 48.2% respectively of the total input to coastal waters around the UK (from DoE and NRA data).

2.6 Other Sources

2.6.1 Mercury and cadmium are ubiquitous elements in the Earth's crust, therefore these metals are naturally occurring trace contaminants of bulk raw materials used in industrial processes and product manufacture. Although the metal concentrations are low the large masses of these materials utilised can result in mercury and cadmium release to all environmental compartments.

2.6.2 Mercury and cadmium are typically released by combustion and tend to be collected by gas cleaning systems into solids destined for landfill.

2.6.3 There would therefore seem to be an opportunity for minimisation of mercury and cadmium release by selecting bulk raw materials which represent the lowest practicable contamination not entailing excessive costs. This concept is expanded in Section 3.

2.6.4 Mercury and cadmium are likely to be found in a household and body care formulations in varying concentrations depending on the source of the precursor materials.

2.6.5 A recent report (Foundation for Water Research 1994) investigated diffuse sources of heavy metals to sewers in two sewerage catchments; Bracknell and Shrewsbury. Table 2.8 shows the relative contribution of the domestic sector to the mercury and cadmium load in sewage.

Table 2.8 Sources of Mercury and Cadmium at Two UK Sewage Treatment Plants

Source	**Cadmium**		**Mercury**
	Bracknell	**Shrewsbury**	**Bracknell**
Domestic	27.1%	30%	41.3%
Light Industry	33.6%	22%	9.5%
Commercial	10.7%	7%	49.0%
Runoff	27.9%	41%	-

2.6.6 At Bracknell, the domestic input for cadmium was resolved further into 16% from washing machines, 11% from dishwashers, 3% from bathing and 70% from faeces. This suggests most of the domestic cadmium is derived from food consumption rather than from household or bodycare products.

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3. MERCURY AND CADMIUM CONTAMINATION OF BULK RAW MATERIALS

3.1 Introduction

3.1.1 In this section we investigate the trace mercury and/or cadmium contamination of bulk raw materials consumed within the UK.

3.1.2 Every year large quantities of mineral commodities are extracted from the ground, or imported into the UK. These minerals serve as raw materials, for example in cement manufacture or non-ferrous metal smelting, or as fossil fuel burnt for energy production. Minerals such as limestone or calcium hydroxide are commonly used in pollution abatement plant to neutralise acidic liquids and scrub acidic gases. Materials such as phosphoric acid are imported and refined for inclusion in fertilisers and detergents. Many industrial processes, particularly those involving heat, can release mercury and cadmium to the environment.

3.1.3 The UK mass flux of mineral commodities that could be contaminated by mercury or cadmium (and other trace metals) is summarised in Table 3.1 from British Geological Survey data (BGS 1992 and 1995).

3.1.4 The trace metal content of the individual minerals as supplied will depend on the local geology and any post-extraction treatment. It is reasonable to assume that considerable variation will be present within individual batches of material from the same source, but statistical sampling methods are available to ensure representative analyses can be obtained for retail or process purposes. It is logical to assume that minerals extracted or imported from different localities will have widely different trace metal contents. An example of this is phosphatic rock imported for phosphoric acid production; phosphatic rock from the USA has an average cadmium content of 6.5 mg/kg, from Morocco or Tunisia 18 mg/kg, but from Senegal 71 mg/kg (Hutton et al. 1987).

3.1.5 We have experienced great difficulty in obtaining typical trace metal concentrations for mercury and cadmium contaminated minerals in the UK. This is due to a number of reasons including;

- bulk mineral suppliers being under no obligation to provide expensive trace metal analysis to purchasers on a "nice to know" basis;
- many mineral extraction companies also being the commodity end-users and having no need of detailed chemical analysis;
- companies being aware of the range of mercury and cadmium in their raw materials and products, but the information is not available due to its commercial or environmental sensitivity.

Other researchers have also found UK mercury content data both sparse and very difficult to obtain (Personal communication BGS).

3.1.6 There is no central repository of information on the mercury and cadmium content of UK minerals by region. The BGS are only now beginning to include mercury and cadmium concentrations in their UK survey work.

3.1.7 The BGS have carried out a pilot hydrogeochemical survey of North Wales for a range of economic and environmental objectives including cadmium, but excluding mercury analysis (Simpson et al. 1993). Dissolved cadmium in stream waters showed a similar distribution pattern to lead. The pilot survey results suggest bedrock geology and mineralisation are the most important variables influencing surface water chemistry, with anthropogenic, atmospheric, seasonal and geomorphological influences being modifying influences. Also regional contamination of surface waters from industrial activities can be detected in data sets.

Hydrogeochemical data can be used as pathfinder indicators for mineral deposits. The BGS are commencing a systematic survey of UK minerals starting in Scotland and working south, however the first information is yet to be published.

3.1.8 The mercury and cadmium content of fossil fuels is discussed separately in Sections 6 and 11.

3.1.9 HMIP guidance notes published in 1993 include reference to the use of purer feedstock to minimise process releases. This concept could be expanded to become an authorization requirement for section A and B processes; that BATNEEC includes a demonstration that the selection of bulk process materials represents the lowest practicable trace metal contamination not entailing excessive cost.

3.1.10 Where bulk minerals are sold or imported, potential purchasers should be in a position to assess the relative contamination of different mineral sources by a certificate of analysis or equivalent. This is analogous to the information required on products sold to the public which require a typical contents analysis.

3.1.11 As information becomes available from IPC applications and maybe from other sources such as the BGS, then the variation of metal content in UK and foreign minerals will become clearer.

3.1.12 Where no sale takes place in the flow from extraction to process, the company would need to demonstrate that the minerals handled were sourced from the lowest contaminated locality, or processed in such a way as to reduce the toxic metals content, for example as in coal washing.

3.1.13 More detailed analysis of input raw materials should also aid the selection and applicability of end-of-pipe pollution control technology.

3.2 Bulk Industrial Chemicals

3.2.1 The widespread presence of trace quantities of toxic metals found in a 1989 survey of industrial effluent (Water Research Centre 1990) suggested that industry was using raw materials containing low concentrations of toxic metals. Some grades of caustic soda from the chlor-alkali industry are well known to be contaminated by mercury, and other chemicals such as mineral acids could be contaminated by cadmium and/or mercury. Trace cadmium concentrations are also likely to be found in printing inks and dyes.

3.2.2 Typical analyses or specifications for retail chemicals are available on request from chemical suppliers. These analyses includes toxic metal concentrations.

3.2.3 Therefore chemical purchasers can select materials which contain zero or minimum mercury and cadmium concentrations. The commitment to purchase materials not contaminated by mercury and cadmium sis now included in IPC Guidance. Water PLC trade effluent consents already contain a clause requiring the trader to inform the Water Company of any changes in raw materials likely to alter the trade effluent nature or composition.

3.3 Fertilisers

3.3.1 Phosphate fertilisers applied to arable land contain cadmium and minor quantities of mercury (Personal communication Fertiliser Manufacturers Association). Fertiliser concentrations in fertiliser were 78.5 mg/kg P_2O_5 and 0.4 mg/kg P_2O_5 cadmium and mercury respectively (based on rock phosphate trace metal content, 1983 data (Hutton et al. 1986). For arable land in 1983, cadmium addition in phosphate fertilisers exceeded that of sewage sludge and atmospheric deposition; for mercury the burden from fertilisers was negligible compared to atmospheric deposition, sewage sludge and pesticide use. The phosphate rock processing produced large quantities of cadmium contaminated gypsum which was dumped at sea.

3.3.2 In 1992 approximately 371,000 tonnes P_2O_5 was applied in the UK at around an average concentration of 40 mg/kg cadmium (Personal communication Fertiliser Manufacturers Association). This is equivalent to approximately 15 tonne per year cadmium. The P_2O_5 content of fertilisers is derived from phosphoric acid as large scale phosphatic rock processing has ceased in the UK, however the phosphoric acid is imported and the cadmium content will vary with source.

3.3.3 There are no specifications for the toxic metal content of fertilisers in the UK. However significant reductions seem feasible by selecting low contamination sources, or introducing cadmium removal technology. The latter is known to have been tested in Europe, but was considered to be prohibitively expensive.

3.4 Bulk Domestic Chemicals

3.4.1 Historically both caustic soda and phosphates have been used in domestic products such as washing powders or bodycare products.

3.4.2 Cadmium concentrations are known to have varied from product to product according to the phosphate source, but the new generation of 'ultra powders' use zeolite softeners, instead of phosphate, which are universally low in cadmium (Foundation for Water Research 1994).

Table 3.1 - 5 Year UK Flux of Mineral Commodities which may contain Mercury or Cadmium

COMMODITY	TYPE	1988 tonnes	1990 tonnes	1992 tonnes	1994 tonnes
Bauxite	Imports				
	uncalcined	330572	263755	312468	249337
	calcined -abrasive	330572	53371		
	- refractory	40562	123429	73784	86770
	Exports				
	uncalcined	376	15	1333	19524
	calcined -abrasive	914	1387		
	- refractory	2830	3372	8431	3696
Cadmium	Production	399	438	383	469
	Consumption	1484	934	715	664
	Imports				
	metal	1157	971	828	872
	pigments	83	42	23	29
	Exports				
	metal	147	621	308	220
	pigments	1418	941	848	909
Cement	Production				
	cement clinker	13701000	13199000	9872000	11508000
	finished cement	16506000	14740000	11006000	12493000
	fibre cement	251000	234700	121100	154100
	Imports				
	Portland cement clinker	1546311	285324	144629	244101
	Aluminous cement	35313	17612	18102	27249
	Portland cement	1154431	2003727	1211031	1321521
	other cement	68152	119545	81594	15208
	Exports				
	Portland cement clinker	501	4209	2128	15862
	Aluminous cement	26242	30999	30176	22433
	Portland cement	54479	213095	341418	354617
	other cement	16048	18514	27648	24456
Chalk	Production	14516000	13129000	9171000	10236000
	Imports	21864	11308	17503	110424
	Exports	21057	26516	69029	58000
China Clay	Production	3276795	3037486	2502224	22530277
	Imports	8265	16925	24520	22320
	Exports	2902034	2596334	2168572	2173888

COMMODITY	TYPE	1988 tonnes	1990 tonnes	1992 tonnes	1994 tonnes
Coal	Production				
	Anthracite	1798000	1945000	2040000	
	Bituminous	102268000	92452000	82453000	
	Total				48971000
	Imports				
	anthracite	803736	633964	860286	1662281
	bituminous	10881160	14156669	19479171	13379119
	briquetted coal	158508	120237	134973	75134
	lignite	11117	54913	19946	5668
	Exports				
	anthracite	286298	508720	396230	271331
	bituminous	1450667	1812866	576652	953479
	briquetted coal	1736965	137050	70451	105168
	lignite	78558	3467	486	1311
Coke & breeze	Production				
	Coke oven coke	7610000	7521000	6397000	6164000
	coke oven breeze	277000	186000	131000	38000
	Imports				
	coke from coal	681499	226575	459824	499192
	coke from lignite	51145	70570	5743	
	Exports				
	coke from coal	410487	294266	196457	310465
Copper	Production				
	concentrate	732	955		
	refined virgin	49250	46991	10363	11078
	refined secondary	74708	74643	31704	35586
	Consumption				
	blister	50198	46888		
	refined	327728	317227	308256	377325
	in scrap for use	132063	126310	83187	88005
Fireclay	Production	1057000	891605	572000	679000
Gypsum	Production	3700000	3100000	2500000	2000000
Lead	Production				
	concentrates	1185	1377	1000	2000
	bullion	34901	42728	42164	36619
	refined primary	172213	155873	198805	191036
	refined secondary	201632	173505	147990	161430
	Consumption				
	refined	302514	301577	263648	267591
	scrap + remelted	37004	32465	38655	38538

COMMODITY	TYPE	1988 tonnes	1990 tonnes	1992 tonnes	1994 tonnes
Limestone	Production				
	limestone	105819000	102641000	89399000	106626000
	dolomite	19861000	20673714	18539236	17616000
	of which for industrial use	2285000	2022000		1397000
	Imports				
	limestone flux				
	lime	4555	11598	24860	2419
		5711	5673	8656	11346
	Exports				
	limestone flux				
	lime	480312	604034	569023	699365
		27194	37373	44496	44466
Mercury	Imports				
	elemental	311	51	67	5
	oxide	71	47	16	26
	Exports				
	elemental	67	176	80	245
	oxide	57		11	18
Natural Gas	Colliery methane	120*	101*	78000*	63*
	Other natural gas				
	landfill gas etc		218	306*	359*
	offshore	39135*	45347*	51387*	64534*
	Condensates	5004*	3612*	5067*	7900*
	Consumption	48428*	50579	54970*	65175*
	Imports				
	liquified natural gas	1089808	1530578	1299614	6669394
	other natural gas	7746971	5537158	4217516	2340135
	Exports				
	liquified natural gas	1960475	1742005	2338158	2642208
	other natural gas	86148	8560	47030	687617
Petroleum	Production				
	crude petroleum	109455000	87992000	89184000	119032000
	condensates	5004000	3612000	5067000	7900000
	refined products	79837000	82286000	85783000	86644000
	Consumption				
	refinery fuel	5484000	5838000	6080000	6256000
	fuel elsewhere	62317000	64774000	64839000	63780000
	not used as fuel	10000000	9169000	10631000	1117800
	Imports				
	crude petroleum	32885988	43748921	47144259	39837795
	partly refined petroleum	20136732	22999915	20416304	19285209
	Exports				
	crude petroleum	63804707	54162184	54388088	77612329
	partly refined petroleum	16919700	19010978	21641470	24478981

COMMODITY	TYPE	1988 tonnes	1990 tonnes	1992 tonnes	1994 tonnes
Phosphorus	Imports				
	phosphate rock	746823	548126	224075	74785
	ammonium phosphate				
	- fertiliser	152009	179366	208568	328369
	- other	437	1292	2244	1095
	superphosphate	251443	382591	282352	294882
	other phosphatic fertilisers	11263	7241	2437	8059
	phosphoric acid				
	calcium phosphate	229390	267071	265797	421925
	sodium phosphates	51335	49191	61799	64943
		28675	19541	18149	35049
	Exports				
	phosphate rock				
	ammonium phosphate	356	677	1642	4857
	- fertiliser				
	- other	7230	5784	6612	10012
	superphosphate	2884	2293	444	2514
	basic slag	67	85	24	40
	other phosphatic fertiliser	26	69	383	810
	phosphoric acids	76	431	187	459
		17175	11797	10536	
Titanium	Titanium dioxide Production				
	Consumption	266290			
		150100	127500	108400	112300
	Imports				
	Ores & Concentrates				
	ilmenite				
	other (rutile)	299561	247902	184458	104384
	Scrap	157342	126713	135730	172846
	Unwrought	12005	9871	8245	8505
	Wrought	2781	4981	4040	5939
	Ferro-titanium	1901	2988	1570	1226
	Oxides	929	1464	5190	7026
	Pigments based on TiO2	3490	2767	18159	10701
	Titanium slag	37962	36051	39931	58747
	Exports	47825	55930	58991	67668
	Ores & Concentrates				
	ilmenite				
	Scrap				
	Unwrought	33	33		23
	Wrought	1432	1058	1770	2906
	Ferro-titanium	387	1192	2432	1968
	Oxides	1270	2452	2164	2943
	Pigments based on TiO2	11857	11244	10591	12825
		33327	26714	13790	11799
		132280	117979	156753	162502

COMMODITY	TYPE	1988 tonnes	1990 tonnes	1992 tonnes	1994 tonnes
Zinc	Production				
	concentrates	5502	6673		
	slab	76028	93309	96813	101300
	Consumption				
	slab	192473	193023	190060	196468
	scrap	51522	52376	46726	45013
	Imports				
	ores & concentrates	187826	278301	185766	243051
	ash & residues	15197	27308	30675	10607
	scrap	6487	5028	2848	3759
	unwrought	134000	123641	122639	124578
	unwrought alloys	4957	4682	2792	5743
	wrought	4053	3922	4654	4948
	Exports				
	ores & concentrates	9330	21927	122	57
	ash & residues	6045	3292	23902	5716
	scrap	25079	25636	23526	26558
	unwrought	7089	7671	13073	18221
	unwrought alloys	6610	11414	13781	21946
	wrought	4785	6789	8419	6804

Source - British Geological Survey 1992 and 1995

* - thousand tonnes oil equivalent

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4. MERCURY, DENTISTRY AND AMALGAM USE

4.1 Introduction

4.1.1 In this section we update mercury inputs and releases associated with amalgam tooth fillings in the UK population with 1995 data.

4.1.2 Firstly, we consider the nature of dental amalgam, its routes into the environment and potential environmental fate. A mass emission estimate follows based on the best available information. Alternatives to the use of amalgam or abatement measures are discussed. Comparisons with other countries are included where appropriate.

4.1.3 The continued use of mercury in amalgam fillings is a unique example of a dilemma representing on one hand the drive to eliminate mercury from the environment, and on the other, the health benefits of cost effective fillings to the population.

4.1.4 When emissions from chlor-alkali plants are eliminated or minimised, mercury from dental amalgam waste will become the largest direct release source to the hydrosphere in the UK.

4.1.5 Mercury release is possible at all stages of the amalgam cycle, however this section concentrates on direct releases of mercury to the sewer, as mixed in dental amalgam from dental premises and from *in vivo* fillings in the population. It does not take detailed account of incidental mercury releases;

- during preparation of amalgam materials;
- during amalgam recovery or mercury recycling;
- from clinical waste incineration or disposal;
- from crematoria or other funeral activities;
- to air during dental surgery activities.

4.1.6 Considerable research has been published addressing the health implications of using amalgam fillings. The health impacts of amalgam restorations on dental workers or the general population are not discussed in this environmental study.

4.1.7 The mass flux of mercury from dental amalgam to the UK environment has been addressed by a number of research studies carried out since 1990 (WS Atkins 1995, ERM 1996, OECD 1995). This work has been carried out against a trend of improving dental hygiene and the effects of potable water fluoridation or fluoride toothpastes.

4.1.8 The number of amalgam fillings placed annually since 1990 has progressively reduced; for example in England and Wales the total number of amalgam restorations has fallen by 21% since 1991/92 (Department of Health) for the over 18 group, as shown by Figure 4.1.

4.1.9 The implications of improved dental hygiene, particularly amongst the younger population, will progressively work through the remainder of the population.

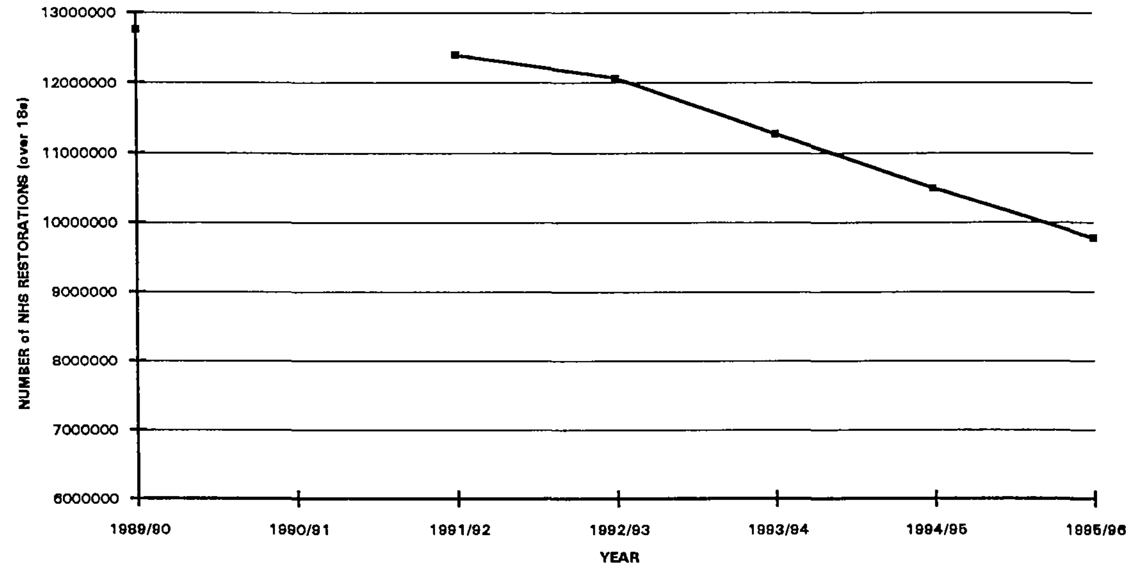


Figure 4.1 - Number of NHS Amalgam Restorations in England & Wales (for over 18s)

4.1.10 Also dental practice methods are changing. New techniques involve minimising the size of cavity prepared for an amalgam insertion, or patching, rather than totally replacing, existing amalgam restorations (Personal communications DoH and British Dental Association).

4.1.11 The trend of progressively reducing dental amalgam placements is likely to continue, at least in the short term, until a new equilibrium is established between improved dental hygiene and number of restorations required. This aspect must be noted when interpreting mass balance information; the UK is in a transient phase at present.

4.1.12 The number of amalgam restorations placed may decrease faster if public awareness of alleged harmful health effects increases, through adverse media coverage for example.

4.1.13 There are many organisations with commercial, health or regulatory interests in the supply, use and release of amalgam from dental surgeries. The implications of large scale changes to the existing situation are complex, costly and beyond the remit of this study.

4.1.14 The primary objective of this section is to describe the nature of amalgam used in filling teeth and how the mercury component is reaching the environment. The mass balance provided quantifies the flux of mercury directly associated with the dental route.

4.2 Dental Amalgam Fillings

4.2.1 Dental amalgam is a heterogeneous mixture of approximately 50 % mercury, 25% silver and the remainder copper, tin and zinc. When the materials are mixed to produce amalgam, a conglomerate of these metals is created which cannot be classified as a true alloy, only as a mixture. In the setting process, crystal-like forms are created with varying degrees of hardness dependent upon which metals the mercury reacts with.

4.2.2 Modern amalgams are prepared from two types of alloy; *conventional silver-tin amalgams* and *high copper amalgams*. The first is prepared from a silver-tin alloy containing small amounts of copper and zinc, whilst the second is prepared from either a mixture of silver-tin and silver-copper alloys (admixed alloys) or from a ternary silver-copper-tin alloy (single composition alloy) (Eley 1993). High copper amalgams have superior clinical properties with a higher resistance to corrosion and marginal breakdown than conventional amalgams (Phillips 1982).

4.2.3 A conventional alloy must contain a minimum of 65% silver, a maximum of 29% tin and approximately 3% copper and less than 1% zinc. High copper amalgams contain 13-20% copper (Osborne et al. 1980).

4.2.4 Throughout this section, **prepared amalgam is assumed to have a 45% mercury content** although the final mercury mass percentage varies with the amount of alloy used to make a clinically acceptable mix.

4.2.5 Reduced mercury dental amalgam capsules are available. One ternary amalgam contains 42.5% mercury and claims a corrosion resistant restoration with good compressive and tensile strength (Kerr Tytin, 1993).

4.2.6 Dentists using Dentomat trituration (grinding together) equipment can vary the relative proportions of mercury and alloy producing different amalgam characteristics to suit individual applications.

4.2.7 Trituration of the alloy powder with triple distilled mercury produces a mouldable plastic mass which quickly sets by formation of new intermetallic compounds. This setting mechanism for conventional amalgam can be summarised as follows:

$$\begin{array}{ccccccccc} Ag_3Sn & + & Hg & \rightarrow & Ag_3Sn & + & Ag_2Hg_3 & + & Sn_{7\text{-}8}Hg \\ (\gamma\text{ phase}) & & & & (\gamma\text{ phase}) & & (\gamma_1\text{ phase}) & & (\gamma_2\text{ phase}) \end{array}$$

The unreacted γ phase particles are embedded in a matrix of γ_1 and γ_2 phase particles (Phillips 1982).

4.2.8 Conventional amalgams are used extensively in the UK. Copper amalgams are virtually obsolete as their only real application was in children (Personal communication BDA). Alternatives now include glass ionomer and composite or synthetic resins.

4.2.9 Triturated amalgam progressively sets with time. The material reaches a compressive strength of 2,800 kg/cm^2 after one hour increasing to 5,600 and 6,300 kg/m^2 after 24 hours and seven days respectively.

4.2.10 Triturated amalgam is prepared immediately before insertion into the prepared dental cavity. The mouldable amalgam is inserted into the prepared tooth cavity where it hardens after shaping by the dentist.

4.2.11 Mercury is a dense material around 13600 kg/m^3. The density of dental amalgam, calculated by combining the densities of the constituent metals in the appropriate ratios, leads to an estimate of 11200 kg/m^3, but triturated amalgam also contains a significant number of interstices which reduce the overall density further.

4.2.12 In one study the density of dental amalgam particles collected by an amalgam separator were assessed from four German and three Dutch dental practices (Muschelknautz 1992). As the samples contained varying amounts of dentine and dental cement in addition to the amalgam, the average solid substance density varied between 2810 and 7450 kg/m^3. For comparison, the density of a German standard amalgam sample was also determined and was found to be 9500 kg/m^3. When the samples were washed with tribromomethane to remove the dentine; the density increased to between 6300 and 10340 kg/m^3.

4.2.13 Dental grade mercury and alloy materials are supplied separately against British Standards BS 4227 (1986) and BS EN 21559 (1992) respectively. Amalgam materials can either be supplied as capsules partitioned into approximately equal quantities of alloy and mercury, or as bulk mercury and alloy powder. Current market shares are approximately 25% for capsules and 75% for bulk chemical supply. Capsules are more expensive than bulk materials. Dentists can buy amalgam materials from dental supply companies in the UK, or mail order from overseas. The diversity of this market has prevented previous studies from obtaining any realistic supply data (WS Atkins 1995).

4.2.14 The quantity of amalgam required for each restoration varies according to the volume of the prepared occlusal cavity.

4.2.15 Amalgam materials can be dispensed as pre-set spills. One spill is equivalent to approximately 400 milligrams mercury and 400 milligrams alloy (a total of 0.8 grams). Two and three spill amalgam materials contain 600 and 800 milligrams of mercury respectively with an approximate equal alloy mass. Alternatively a dentist will formulate an amalgam mix to his own specification.

4.2.16 During conservation work, the dentist will request an appropriate amalgam mass.

4.2.17 As successive studies have shown, there are no "typical" data on the average size of amalgam restorations placed. Mercury masses between 0.6 and 1.25 grams have been suggested. A Canadian estimate (Vimy 1995) was 750 to 1000 mg mercury per restoration. Another range estimate is 0.49 to 1.12 grams amalgam placed (personal communication DoH). Anecdotal evidence from dental sources suggest a typical triturated amalgam prepared for insertion is two spill; i.e. around 600 milligrams of mercury.

In the absence of reliable amalgam material supply data, there is no reliable quantification of the average amalgam restoration size and starting amalgam mass. Until knowledge in this area can be improved, all mass balance estimates will be open to challenge.

4.2.18 In general, most amalgam fillings are performed by NHS dentists rather than private dentists. Therefore there will be regional differences in the quantity of amalgam restorations performed broadly according to the distribution of NHS or private practices. Social factors will also affect regional differences.

4.2.19 Dentists claiming from the NHS treat more patients than those in the private sector; a dentist may treat 30 - 40 NHS patients a day whilst a private dentist will probably treat around 10 patients a day.

4.2.20 It is fair to say that amalgam remains the profession's first filling material choice for widespread restorations on the basis of cost, longevity and flexibility.

4.3 Mercury release *in vivo*

4.3.1 There is published evidence showing trace mercury releases from amalgam restorations in the mouth reach the environment either in tidal air or voided in urine or faeces.

4.3.2 The release of mercury vapour from amalgam fillings in the mouth has been known for a considerable period of time (Stock 1939) and has caused concern in various circles. Release of mercury vapour in the mouth has been shown to lead to increased uptake by body tissues and subsequent elimination in urine or via the lungs (WHO 1991).

4.3.3 The release rate of mercury vapour increases dramatically in the mouth when amalgam surfaces are stimulated by continuous chewing, reaching a plateau within 10 minutes. After cessation of chewing, it takes about 90 minutes for the mercury release rate to decline to the pre-chewing basal value. Hot liquids also increase mercury release.

4.3.4 The *in vitro* corrosion rate is increased if the surface is abraded, hence the increased mercury vapour loss seen following chewing. This is attributed to disruption of the passive surface layer, re-passivation occurring relatively slowly. Amalgam particles accounted for most of the mercury loss of 10 μg/cm^{2}during a cyclic (to simulate chewing) loading of 20 minutes duration. The amount of ionic mercury released was estimated to be 3 μg/cm^2 (Brune et al. 1985).

4.3.5 Radioactive tracer work (Frykolm 1957) showed that the insertion of amalgam fillings in the mouths of both dogs and humans resulted in significant increases in mercury concentrations in urine and faeces. In humans, the concentration of urinary mercury increased over a 5 day period following the insertion of 4-5 small occlusal fillings. A new, higher peak occurred a couple of days after the removal of these fillings. Faecal elimination showed a similar pattern, appearing on the second day after insertion with a maximum 1-2 days after removal.

4.3.6 Other workers have shown a relationship between urinary mercury concentration and the number of amalgam surfaces in the mouth. One study (Jokstad et al 1991) showed around 4.8 μg/l more mercury present in urine from individuals with amalgam restorations compared to those with none. Up to 12 μg additional mercury was absorbed per day when more than 36 amalgam surfaces were present. On the basis that 50% of the mercury exposure is excreted in urine, an average loss of mercury is 5 μg per day per person with amalgam restorations.

4.3.7 Another Swedish study (Skare 1995) monitored the gross mass mercury flow balance in 10 individuals. The results are shown in Table 4.1 for individuals on a typical Swedish diet.

Table 4.1 Emission and Excretion rates of Mercury from Amalgam carrying Individuals

Variable	Amalgam loaded individuals		Control individual
	Mid value	Range	
Number of amalgam surfaces	40	18 - 82	0
Oral air Hg° emission	29 µg/d	20 - 124 µg/d	0 µg/d
Urinary Hg excretion	4.5 µg/d	1.8 - 19 µg/d	0.4 µg/d
Urinary Ag excretion	1.7 µg/d	1.4 - 6.0 µg/d	1.3 µg/d
Faecal Hg excretion	64 µg/d	27 - 190 µg/d	1.0 µg/d
Faecal Ag excretion	33 µg/d	11 - 97 µg/d	4.0 µg/d

This study also noted urinary excretions in excess of 15 µg/d were unusual and associated with individuals with a large number of amalgam surfaces in very poor condition.

4.3.8 The reaction of amalgam with chemical species in a surrounding liquid produces both soluble and insoluble corrosion products (Langan et al. 1987). Mercury dissolution from amalgam *in vitro* has been studied using distilled water, isotonic saline and saliva as liquid media (Takaku 1982, Takaku 1985, Kuc 1981, Okabe 1987). The mercury dissolution into mixed saliva *in vitro* had a mean value of 0.853 ± 0.423 µg/ml. The cumulative dissolution after six months ranged from 0.001 - 0.003 µg/ml in water to 0.003 - 0.088 µg/ml in 0.5% sodium chloride (Kozons 1982); on a surface area basis, the dissolution of three types of amalgam after 7 days in 0.9% sodium chloride ranged from 0.50 2.21 g/cm^2.

4.4 Dental Surgery Release Routes

4.4.1 Waste amalgam is released from the surgery from six main sources;

- in extracted teeth containing amalgam restorations;
- as contamination of packaging or consumables such as swabs, clothing etc.;
- as surplus triturated amalgam from mixing fresh fillings;
- from decontamination of instruments and other reusable equipment;
- from shaping new restorations;
- as amalgam grindings from removing old conservations.

Another source may be accidental mercury spillage, however spillage kits containing a mercury absorbent paste are recommended for this eventuality (BDA Advisory Service 1993).

4.4.2 Mercury vapour is released to the surgery atmosphere during trituration, amalgam handling, shaping and drilling. Some of this inorganic mercury will be absorbed into the patients or dentist's body. This will be excreted or exhaled.

4.4.3 Extracted filled teeth and contaminated packaging etc. are most likely to be consigned to clinical waste for disposal and are therefore not included in our estimation.

4.4.4 Surplus triturated amalgam is inevitable as every restoration requires an excess to be prepared. However, surplus amalgam mass is minimised by preparing specified quantities to order only and unnecessary waste is a cost penalty for the dentist. Residual triturated amalgam in the mortar (or equivalent) is easy to dump into a receptacle for recycling and protection of surgery staff.

4.4.5 During restorations, mouldable triturated amalgam inserted in the prepared cavity is carved to shape. Carved amalgam pieces are removed by suction, swallowed or deposited in the spittoon.

4.4.6 Removal of old amalgam restorations represents the largest mass of amalgam waste from dental premises. Mechanically removing old restorations produces very fine particles as the old filling is essentially pulverised to dust.

4.4.7 Recent changes in dental practice encourage the patching of damaged amalgam restorations rather than total replacement.

4.4.8 Drilling old restorations produces a fine dust/aerosol that is deposited on/in the patient, the surgery workers and equipment. Contaminated burrs, cannulas and other equipment are routinely cleaned with a wire brush before autoclaving. This activity is likely to be carried out over a hand basin or the spittoon.

4.4.9 The primary paths by which waste amalgam material leaves the surgery are;

- from the patients mouth via the suction system removing saliva, blood, dental materials and amalgam;
- from the spittoon;
- from surgery hand basins;
- excess from the trituration vessel (recycled).

4.4.10 Minor amounts will be ingested or inhaled by the patient/dentist to be voided in the breath, faeces or urine later.

4.4.11 The primary routes by which mercury (in any form) routinely leaves the dental surgery are summarised by Figure 4.2.

4.4.12 In wet suction systems, amalgam particles and other organic debris are flushed by water sprays in the mouth. Accumulated water and debris is sucked out via small bore cannulas and pipe work. Flow from the spittoon is also diverted to the suction system. The resulting water/air/debris mixture passes through coarse filters to trap large debris, through a suction pump and to the foul drainage.

4.4.13 Dry suction systems collect and remove water droplets, together with amalgam particles and other debris from the mouth and spittoon. The water/air/debris mixture passes through coarse filters and fine filters and a phase separator. The air fraction goes to the suction pump and is exhausted from the surgery; the liquid fraction passes to sewer.

4.4.14 Sedimentation bowls to retain amalgam particles are often fitted in modern dental chair equipment.

4.4.15 A suction system may serve a single dental chair, or multiple chairs especially in teaching hospitals.

4.4.16 Historically, wet collection amalgam separators were preferred (on cost grounds), however recent developments in dry systems have significantly reduced capital costs. Dry systems are now substantially cheaper than equivalent wet systems and this may influence abatement equipment selection in the UK.

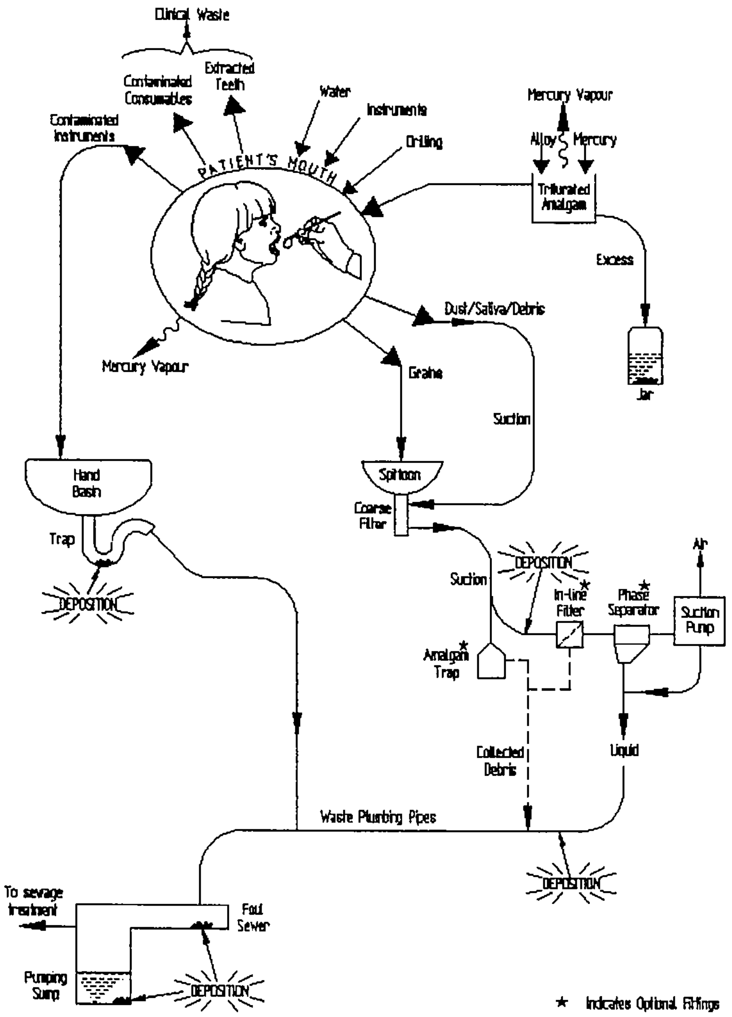


FIGURE 4.2 - SURGERY ROUTES (without amalgam separator)

4.5 Surgery Emission Particle Size Distribution

4.5.1 Dental amalgam waste is released from dental surgeries in a range of particle sizes varying from relatively large chunks to fine dust particles from drilling or carving. Usually amalgam particles are associated with a matrix of organic matter including saliva, blood, dentine and cement.

4.5.2 Various assessments have been made of amalgam particle size distribution although in reality each surgery release is likely to vary according to the dentist's working method and other local factors.

4.5.3 Currently the German standard particle distribution, for use in assessing amalgam separator efficiency, is under consideration for international (ISO) acceptance. The size distribution is shown in Table 4.2.

Table 4.2 - German particle distribution standard

Fraction	Size (mm)	Mass (g) in 10 g sample
1	3.0 - 0.5	1.6
2	0.5 - 0.1	0.4
3	< 0.1	8.0

4.6 Waste Amalgam at the Dental Surgery

4.6.1 Heavier amalgam particles will sediment wherever insufficient water velocity exists to suspend. The deposition rate (ie. settling velocity) varies with the particle size and density. Deposited material will be associated with other organic debris and bacteria present leading to the formation of a plastic, sticky, dense matrix or film which is difficult to remove.

4.6.2 Once amalgam has entered the waste plumbing pipe work or the sewers there are several possible scenarios as follows;

- particulate amalgam waste is washed through to the sewage treatment works with no or minimal soluble mercury release en route. There is partial particle removal during grit separation with the remainder sedimenting in the settlement tanks; i.e. waste amalgam is benign in environmental terms;

- amalgam waste particles accumulate in pipes with no or minimal soluble mercury release forming a relatively inert benign deposit;

- amalgam waste particles are washed through to the sewage treatment works where there is partial removal during grit separation and sedimentation processes; there is a significant amount of soluble inorganic mercury release;

- amalgam waste particles accumulate in pipes and sewers with a significant amount of soluble inorganic mercury release;

- amalgam waste particles undergo reactions in the pipe work and sewer environment to produce a variety of soluble and/or insoluble mercury compounds.

4.6.3 The important implications of the dense nature of amalgam are ;

- that anecdotal evidence suggests it will sediment readily and requires a high water velocity to move deposited material which is probably stabilised by an organic debris/biomass matrix;
- that separation of amalgam from other dental debris by gravity is possible; either in a simple trap, or mechanically in a centrifugal or cyclonic separator.

4.6.4 Within the dental industry it is widely known that waste amalgam material sediments;

- within the suction system hoses at low points; especially if surplus flexible hose is coiled (above ground pipe work);
- in filters and traps;
- in the plumbing pipe work after the suction system prior to the sewer (in below-ground plumbing pipe work).

4.6.5 In most cases, technicians clear suction systems for dentists, either routinely or on demand when suction is compromised. Large (unspecified) quantities of amalgam are known to have been removed from suction systems by technicians in the past (and this practice must continue today). This material is/was left at the surgery for the dentist to dispose of, or retained and sold for recycling by the dental technician. Alternatively, it could be flushed from the system.

4.6.6 When blockages occur in below-ground pipe work, these are typically cleared by either a plumber or drain cleaning contractor. This would inevitably involve rodding, blowing or flushing deposits to sewer.

4.6.7 Typically there are a range of coarse filters fitted in dental equipment e.g. below the spittoon. The primary function of such filters is to catch valuable materials and protect the suction pump.

4.6.8 Suction line filters and traps need to be cleaned intermittently. Any amalgam material recovered is mixed with blood, saliva or other debris and is infectious and obnoxious. The fate of such amalgam material is unclear; it could be added to the recycling receptacle or washed away to the sewer by another means.

4.6.9 There are practical difficulties in measuring mercury release to sewer from dental surgeries as amalgam is released to the sewer in a range of particle sizes. The ultimate fate of these particles will be related to size and density; heavier particles can accumulate in sink traps and surgery drainage, in non-turbulent sewerage and in sumps or grit traps, whereas fine particles may reach primary sedimentation processes or secondary treatment at sewage treatment plants. Soluble mercury species will reach the liquid stream at the sewage treatment works.

4.7 Chemistry of Amalgam in Water

4.7.1 In the case of immediate releases from dental sources, the mercury exists in two main forms;

- combined in amalgam particles, usually within a matrix of dentine debris;
- as dissolved inorganic mercury leached from the amalgam particles.

Subsequent reactions undergone by any mercury present in a system are strongly dependent on a large number of factors including;

- pH;
- oxidising/reducing conditions;
- presence/absence and type of any microfauna and flora (biofilm);
- other chemicals present; these could inhibit/promote corrosion and, if the latter, could result in the formation of soluble or insoluble products.

Any of these factors can change rapidly within a short distance or timescale. So the sediment micro-environment can be considerably different from the bulk liquid.

4.7.2 One study (Callmander et al. 1986) evaluated the efficiency of a Millipore AP 40 filter and an amalgam separator in reducing mercury discharge to sewer from an actual dental practice. Residual mercury (i.e. not captured by the control devices) was between 0.8 - 2.1% of the input load and was found to consist of;

- 63.3% amalgam particles;
- 21.1% soluble metallic mercury;
- 15.6% ionic mercury.

4.7.3 In uncontrolled discharges, larger amalgam particles will account for a much higher percentage and so it is not possible to calculate any values for the relatively small discharges of the soluble and ionic mercury to sewer.

4.7.4 However, even if the majority of the mercury remains intrinsically bound and unavailable for further reaction, there is a small portion existing in a chemically reactive state that could undergo further reactions with microorganisms or other chemicals present.

4.7.5 Mercury release from freshly triturated amalgam is a recognised hazard. Safety instructions supplied by the manufacturer (Ivoclar-Vivadent) state that; "danger to the dentists and dental personnel from mercury vapour may be avoided by...storage of the amalgam residue under water or, even better, fixing solution in well-closed containers". The American Dental Association recommends that it be 'stored under a small amount of photographic fixer in a closed container'.

4.7.6 Any studies on mercury release under sewer conditions must differentiate different mercury compounds; for example dissolved inorganic, organo-mercury species and mercury associated with amalgam particles or other suspended solids.

4.8 Amalgam Waste in the Sewers

4.8.1 Evidence concerning the solubility of the mercury constituent of the amalgam is contradictory and so it is not yet clear to what extent mercury in set amalgam can become bioavailable following release from the surgery (Arenholt-Bindslev1992). For example; '..there is no conclusive research which proves that the mercury constituent of amalgam particles becomes bioavailable and enters the food chain' (Rodgers 1989). Another paper states that '..small amounts of mercury..can pass the barrier of the waste water treatment plant as ions or organic mercury compounds and are released into the drinking water and the food chain' (Fischer et al. 1989).

4.8.2 Fine amalgam particles have a high surface area/volume ratio presenting a high surface area for reactions. Newly triturated amalgam may not be fully hardened on release from the surgery (i.e. for safety, surplus triturated amalgam must be retained beneath liquid to prevent mercury vapour release). Therefore soluble mercury release from amalgam particles under sewer conditions is possible, but not proven.

4.8.3 In the sewer, corrosion is strongly dependent on the chemical and physical conditions present; e.g. abrasion, temperature, pH, presence of detergents (phosphates), types and concentrations of ions present (Moberg et al. 1991). However, *in vitro* investigations on the solubility of amalgam suggest that in pure water and sewage, only negligible amounts of mercury (less than 0.01%) are released (Heintze et al. 1983, Beckert 1988).

4.8.4 One UK survey (Foundation for Water Research 1994) found higher sewage mercury concentration (0.43 µg/l) from a catchment containing dentists compared to samples taken from premises without dental inputs (0.25 µg/l).

4.8.5 This survey showed that a sewer catchment with dental premises contained up to four times the mercury concentration derived from a modern housing estate. Unfortunately, this study did not define whether this mercury concentration was total or soluble. This survey also recorded a discrepancy between mercury load at the sewage treatment works and the catchment mercury inputs measured. Such an input shortfall may be partially explained by sampling error, or by amalgam deposition within the dental premises and the sewerage system. Also leaching from *in vivo* fillings would contribute a background concentration.

4.8.6 A Danish study measured the mercury burden in waste water samples collected from 20 general dental clinics in one working day (Arenholt-Bindslev 1992). There was a very wide variation in output; from 24 - 1700 milligrams per day. Clinics fitted with 'Swedish-approved amalgam-separating devices' had lower values; the highest of which was about 190 milligrams per day. Data were then correlated with the number of full-time dentists working at each clinic; this gave a range of loads of 12 - 837 milligrams mercury per dentist per day. Further extrapolation produced an estimate of the burden on a yearly basis; up to 200 grams mercury per dentist per year. These data correspond well with previous results from German studies and Swiss estimates, all of which were based on data from fewer clinics.

4.8.7 Data from other studies investigating sewage from clinics with separators have demonstrated that the mean mercury level in waste water is about 10% of the values found in clinics without separators (Arenholt-Bindslev et al. 1990, Hogland et al 1990). The type of separators are not specified however, the standards in countries where separation is mandatory demand 95-99% separation efficiency.

4.8.8 Two studies (Arenholt-Bindslev et al. 1990, Hogland et al 1990) concluded that there is no correlation between the amount of amalgam work performed in a clinic during a waste water sampling period and the quantity of mercury found by waste water analysis. Their findings indicated that the amalgam particles sedimented in tubes or drains within the clinic and thus were continuously released by the water stream over a period of time.

4.8.9 It is commonly known that inorganic mercury can be transformed into various soluble or volatile organic forms, such as methyl-mercury (Jensen et al. 1969, Feldmann et al 1995) or dimethyl-mercury (Snow 1993) by microorganisms in sediments or sewage treatment processes. Subsequent investigations have revealed that methylation occurs under a variety of conditions including aerobic and anaerobic waters (USEPA 1984). Methylation and de-methylation may also occur in the human gut.

4.8.10 It is conceivable therefore that bacterial action in the sewer and drainage systems could transform soluble metallic or ionic mercury released from amalgam particles. By virtue of their size, fine amalgam particles present a very large surface area for attack by corrosive or chemical processes.

4.8.11 A Swedish study (Ekroth 1978) in which dental amalgam grindings (0.5 grams per litre) were added to aquaria for 28 days found that mercury concentration in the fish livers increased by a factor of 60. The metallic mercury in the amalgam was oxidised to Hg^{2+} which was biotransformed to methyl-mercury, a form that was readily absorbed by the fish.

4.8.12 The validity of these results has been questioned ((Arenholt-Bindslev 1992) as the amalgam used was of the γ_2 variety which is known to corrode readily and which is banned in Germany (Jones 1993). However, conventional amalgam containing the γ_2 phase is used extensively in the UK (personal communication BDA).

4.8.13 A Japanese study (Yamanaka et al. 1982) investigated mercury pollution from dentists by analysis of waste water, soil and sludge. Mercury in the waste water was adsorbed and concentrated to high levels in soil and sludge. The results showed that a large amount of amalgam was contained within the drain pipes; when five litres of water was flushed through the system, mercury concentrations in the waste water were higher than when the waste water was sampled undisturbed. When the waste water mercury levels in the final drains of a dental college were low; ranging from undetectable (< 0.05 µg/l) to 6.2 µg/l, the corresponding concentrations found in the drain pipe sludge ranged from 12 - 1900 µg/g on a dry weight basis. In some discharges from dental practices, sludge in the final drain pipe had even higher values; 10200 - 11000 µg/g.

4.8.14 The above study also used gas chromatography to analyze the soils and sludge for methylmercury. This compound was only detected in one instance; a soil sample soaked with waste water from a dental practice where a sewer system was absent. In this instance total mercury was 4100 µg/g whilst the methylmercury was 0.28 µg/g. The detection limit for methylmercury was 0.01 µg/g. The authors therefore concluded that there was no risk that the inorganic mercury discharged from dental practices would be converted to methylmercury in soil and sludge.

4.8.15 Methylmercury concentrations in sewage are understood to be significant in some cities in America, we have not established whether this is related to dental premises.

4.8.16 In summary, there is considerable uncertainty regarding the fate of particulate amalgam waste in the sewer environment. At best the amalgam particles are relatively benign eventually reaching the waste water treatment facility for landfill, surface spreading or incineration. At worst, mercury released from the amalgam particles is transformed to organic mercury species which are significantly more toxic to Man either directly or indirectly through the food chain culminating in fish.

4.9 Fate of Amalgam Waste at the Waste Water Treatment Plant

4.9.1 The chemistry of the amalgam particles in the sewers is uncertain. Denser amalgam particles almost certainly will sediment as grit at the treatment plant inlet, whereas the fine particulate mercury will sediment into the sludge derived from primary sedimentation. Mercury can solubilise from amalgam (albeit slowly), but the rate and requisite conditions are not known. Mercury in solution will associate reversibly with organic matter and is likely to reach the sludge stream at some point.

4.9.2 At the waste water treatment plant, at least 55% of the soluble, colloidal or absorbed mercury passing preliminary treatment will be retained in the sewage sludge (Lester 1983). In the majority of cases, treated sewage sludge is either deposited on agricultural land (stabilised by anaerobic digestion), incinerated or dumped as landfill. In the case of anaerobically digested sludge, mercury is likely to be present as a sulphide during land application, however oxidation to sulphate could release mercury. If the sludge is incinerated, all the mercury present will be released to the flue gas stream and release will be proportional to the efficacy of mercury removal in the scrubbing system.

4.9.3 Mercury derived from dental amalgam reaching the waste water treatment facility will partition between the different flow streams as;

- grit and detritus disposed of to landfill in most cases; mainly particulate amalgam;
- treated effluent from the facility reaching controlled waters; consisting of soluble, colloidal or solids-related species;
- sewage sludge reaching agricultural land or landfill; particularly fine particulate or solids-related (i.e. adsorbed to organic material, or incorporated in biomass);
- volatile organo-mercury atmospheric emissions from the treatment facility.

4.9.4 A discussion of the fate of mercury at sewage treatment works is given in Section 14.

4.10 Waste Amalgam Storage and Recovery

4.10.1 Clean triturated amalgam is easy to collect and store safely in the surgery under water, photographic fixer or potassium permanganate solution. Consequently it is in demand from companies who wish to collect it and extract the silver content.

4.10.2 The amalgam/organic debris matrix recovered from the suction line filters or traps is an unpleasant material which constitutes a health risk. Scrupulous dental assistants may retrieve this material and add it to the excess triturated amalgam receptacle, however, others may simply flush this material to sewer.

4.10.3 In mainland Europe, the mandatory use of amalgam separators has resulted in the introduction of a postal system whereby full receptacles are returned to specific companies for safe recycling (Personal communication Metasys). Dentists are credited with the market value of the recovered metals which is offset against the purchase of a replacement collection canister.

4.10.4 In the UK, this system does not exist although the Post Office has approved the posting of full Metasys receptacles on a national and international basis (Personal communication Metasys). However, the Environment Agency are actively considering the issue of collection, transportation and storage of amalgam waste (personal communication Environment Agency).

4.10.5 In the UK, any collection scheme would need regulation to ensure that all amalgam, including materials from waste pipes, is recovered by licensed routes.

4.10.6 The collection, handling and treatment of scrap amalgam from dental premises is a grey area in regulatory terms. Although the scrap amalgam has a value, it is still arguably a controlled waste (or even a special waste) and as such Duty of Care requirements apply.

4.10.7 A professional publication (BDA Advisory Service 1993) presents current health and safety law in a dental context. A complete section is devoted to guidelines for handling mercury and covers;

- personal hygiene;
- working environment;
- operative procedures;
- storage;
- disposal of waste and contaminated materials;
- spillage; and
- routine monitoring.

4.10.8 The document states that mercury from (spillage or) amalgam residues 'should be stored in a cool place in a well sealed, clearly labelled container under a solution of 5% potassium permanganate or radiographic fixer' until 'sufficient has accumulated for return to the supplier for the purpose of recovery'. The BDA encourages the use of pre-portioned amalgam capsules and further states that 'used capsules should be resealed and disposed of with the clinical waste'.

4.11 Waste Amalgam Abatement Systems

4.11.1 Amalgam sedimentation traps have been fitted in some suction systems for at least five years by several of the equipment suppliers.

4.11.2 The common separation principle is to use the high amalgam density to separate particles from saliva, tooth debris and other materials in the liquid flow.

4.11.3 At best, an amalgam trap consists of a suspended bowl of around one litre capacity, however, most traps fitted are smaller than this. The suppliers recommend emptying the trap every two months.

4.11.4 The efficiency of sedimentation traps is related to the particle size distribution, the capacity and how often the trap is cleaned out. In most cases an efficiency of 75 to 80% removal of inlet amalgam is claimed, although one company claimed up to 90% efficiency. We have no evidence to substantiate this, but the circumstantial evidence of sedimentation in pipes suggests this could be realistic.

4.11.5 The advantage of this crude trap type is low cost. The major disadvantages are no active amalgam level detection (which means a regular cleaning routine is necessary to prevent sediment loss) and that removal performance is unlikely to reliably meet the proposed ISO standard of 95% removal efficiency of input standard. Acceptable performance standards for separators is currently an area of international debate.

4.11.6 Mesh filters are also typically found in suction lines, but the relatively coarse apertures can be expected to retain only larger particles.

4.11.7 Amalgam separators are mechanical devices installed at the dental clinic to recover waste amalgam particles from the surgery effluent preventing transmission to the sewage treatment works. The captured amalgam can be recycled and the cleaned effluent released to sewer or vented externally. Separators are required to achieve in excess of 95% removal efficiency for amalgam particles (Personal communication Durr).

4.11.8 The differences between generic separator types are performance efficiency, cost and amalgam level detection method in the collected material reservoir.

4.11.9 Amalgam separators must be fitted prior to the sewer and treat amalgam bearing streams from the mouth and the spittoon as a minimum. The separating device may be fitted in the dental unit close to the spittoon, or remotely especially if a centralised suction system is used.

4.11.10 Obviously the closer the separator is fitted to the dental chair, the less the deposition potential in the suction system and drainage pipelines.

4.11.11 Mechanical amalgam separators may be small units treating a single dental chair output, or can be centralised units treating discharges from a number of dental chairs at a clinic. The separator may be a combination system with the suction pump, or may be fitted as a separate unit. There are currently two types of amalgam separators commercially available for wet and dry line systems.

4.11.12 Mechanical amalgam separators have been compulsory in some European and Scandinavian countries for a number of years. However, without compelling legislation, supply and installation of amalgam separators in the UK has been very slow probably due to the relatively high cost of the equipment.

4.12 Mechanical Separators

4.12.1 The environmental impact of dental amalgams, whether real or precautionary, has resulted in amalgam separators being made mandatory in Germany, Denmark, Sweden and Switzerland.

4.12.2 Holland has notified the EU of impending regulations concerning installation of amalgam separators; this is in the obligatory consultation period under 83/189/EEC, care of the DoE and DTI (personal communication DTI).

4.12.3 Norway has also notified the EU of impending regulation to install amalgam separators at dental clinics and that amalgam sludge are considered as hazardous. Other aspects specify that amalgam waste shall be collected when cleansing drainage pipes (implying deposition in drainage system is a tangible problem).

4.12.4 Mechanical amalgam separators are available from manufacturers or through dental supply companies. Separators are fitted as integral units within the dental equipment, or as separate units. Larger units capable of treating waste from centralised suction systems taking up to two dental chairs are available.

4.12.5 Although UK retailers and equipment suppliers sell or include mechanical separators in surgery equipment, all the mechanical separator designs are manufactured abroad.

4.12.6 Most mechanical separators supplied to the UK meet the German standard for a minimum of 95% removal efficiency with level detection in the amalgam reservoir. Higher efficiencies are claimed for separators; removals of up to 99.8% are quoted. Furthermore, the units emit an audio/visual signal at 95% capacity followed by an interlocked dental system shutdown at 100% capacity.

4.12.7 In Europe, the full amalgam reservoir is removed, disinfected, sealed and posted to a recycling centre. In the UK, a system to recovery amalgam waste would need to be established or integrated with the existing commercial operations.

4.12.8 The relatively low water flow handled by separator units precludes connection of other contaminated sources such as wash basins. Any regulation of surgery activities will require prohibiting contaminated equipment cleaning except over the spittoon.

4.12.9 There is uncertainty regarding the actual number and location of separators supplied in the UK. Equipment suppliers have installed separators with new chairs of which the separator manufacturers are unaware. However, the number of operating separators overall in England and Wales is probably less than three hundred.

4.12.10 Existing separator installation in teaching hospitals: fitted as part of the rolling equipment replacement programme, are being appraised for mechanical reliability but no performance monitoring is understood to be taking place.

4.12.11 Some Water PLCs and the Water Services Association (WSA) are active addressing the issues of dental amalgam release in England and Wales. The WSA has produced a draft code of practice for dental premises including a requirement for amalgam separators (although this is not public domain at present). Other Water PLCs have been actively monitoring mercury concentrations in sewage sludge and assessing the current situation, but no regulatory action has occurred yet. In Scotland, East of Scotland Water are implementing a monitoring programme for dental discharges potentially leading to regulatory action.

4.12.12 On the basis of the German and Swedish work, the mercury burden reaching the sewer system from dental practices could be reduced by up to 95% if amalgam separators, with the associated recycling infrastructure, were installed in all UK dental practices.

4.13 Number of Dentists in UK

4.13.1 To practice in the UK, dentists must be on the Dental Register of the General Dental Council. In 1994, there were 27,617 registered dentists although some will be retired or working overseas. In 1994, 21,560 registered dentists were located in England and 1,179, 2,623 and 931 in Wales, Scotland and Northern Ireland respectively (Personal communication Dental Practice Board 1995). The number of dentists registered has been steadily increasing since 1960 (16,279 to 27,617).

4.13.2 The current number of practising dentists in the UK is probably between 18,000 and 20,000 (Personal communication BDA).

4.13.3 Included in this figure are approximately 2,000 truly private dentists in the UK. Many dentists perform a mixture of NHS and private work.

4.13.4 Not all dentists perform amalgam restorations. Orthodontists and other dentists do not routinely perform amalgam restorations. Statistics on how many orthodontists or other categories of non conservation dentists were not obtained in this study.

4.14 Dental Mercury Mass Balance

4.14.1 Estimating the mass flux of mercury entering, leaving or recycling in the dental health arena is a complex matter. Statistics available tend to be incomplete, for example private dental restoration activities are not recorded although National Health work is.

4.14.2 The primary unknown factors are;

- the mercury content of dental surgery clinical waste;
- the amalgam mass collected and recycled;
- the average amalgam restoration mass;
- how many restorations are replacements;
- the amount of triple distilled mercury consumed annually;
- the amount of amalgam placement carried out by non-NHS claiming dentists; for example private dental work, teaching hospitals, community dentists etc..

4.14.3 Other factors can be estimated based on statistical information or using simple logic.

4.14.4 The primary information available is the annual number of amalgam restorations placed by dentists claiming from the NHS.

4.14.5 Therefore the mass balance is based on manipulating the number of amalgam restorations known to have been placed annually in the UK.

4.14.6 Our mass balance is based on a mixture of data and assumptions elaborated in text. The result will be some overestimates and some underestimates. Therefore the net result is expected to be a reasonable estimate of the mercury flow through the dental route.

4.15 Number of Amalgam Restorations

4.15.1 There are a large number of restorations carried out annually in the UK. Statistics are available from;

- the Dental Practice Board (England & Wales) - DPB;
- Dental Practice Division (Scotland) - DPD;
- Central Services Agency (Northern Ireland) - CSA;
- Ministry of Defence - MoD.

4.15.2 Restoration data obtained from a number of sources is summarised in Table 4.3. The data collection method changed after 1989/90 when children were removed from the DPB data set (as per capita payments were introduced).

Table 4.3 - Annual Number of Restorations Performed in UK

Year	Number of Amalgam Fillings						Non Amalgam TOTAL[5]
	DPB[1]	DPD[2]	CSA[3]	MoD[4]	Deciduous fillings	TOTAL	
1987	-	1,848,365	560,000				
1988	16,730,980	1,734,882	630,000				
1989	15,580,260	1,739,662	660,000		892,180	17,979,922	7,788,000
1990	-	1,660,540	720,000				
1991	12,395,314[6]	1,436,537	-				6,286,872
1992	12,064,600[6]	1,407,860	715,000				6,490,611
1993	11,268,052[6]	1,393,623	665,000	139,000			6,375,329
1994	10,491,657[6]		575,000				6,401,479
1995	9,774,763[6]	1,364,000E	500,000E	111,000E	669,000E	12,418,763E	6,412,285

Notes:
1: DPB statistics are financial year.
2: DPD statistics are January-December for 1987-90 and financial year for 1991-92 and 1993-94.
3: CSA statistics are as of 1 July each year.
4: MoD statistics are financial year.
5: England and Wales only.
6: Over 18s restorations only.
E: Estimated.

4.15.3 A recent complete analysis of fillings by type and age-group for England and Wales 1989/90 is given in Table 4.4.

Table 4.4 - Breakdown of fillings in 1989/90 (DPB 1990)

Filling Type	Permanent Fillings Over 18s	Permanent Fillings Under 18s	Fillings Deciduous Teeth	TOTAL
Amalgam	12,758,330	1,929,750	892,180	**15,580,260**
Glass ionomer	-	-	932,090	**932,090**
Composite	4,620,560	414,600	39,930	**5,075,090**
Silico phosphate	1,622,840	126,430	-	**1,749,270**
Other	-	-	31,550	**31,550**
TOTAL	**19,001,730**	**2,470,780**	**1,895,750**	**23,368,260**

4.15.4 Restorations are also carried out at the twelve teaching hospitals in the UK, however, no statistics are available for dental training activities. Teaching hospitals also practice conservation work on extracted teeth and other teaching aids, thus adding to the amalgam releases.

4.15.5 Statistics supplied by the Dental Practice Board give the number of restorations performed in England and Wales on a yearly basis. They only relate to dentists providing National Health services in the High Street and not to community practices or those in hospitals. An estimate by a DoH source suggested that community and hospital dentists could account for as much as an additional one tenth of the Dental Practice Board estimate. However, these dentists would be performing fewer restorations than the High Street practices. So we have introduced an annual allowance of 500,000 amalgam restorations to cover these other activities.

4.15.6 We have not been able to estimate the numbers of dentists performing restorations privately as there is no need for these figures to be declared. This sector will perform far fewer amalgam restorations than the NHS, but as the numbers of dentists in private practice are continually increasing, this figure may become increasingly significant over time. For the purposes of this investigation, we have estimated that 250 amalgam restorations are performed annually per private dentist, however we cannot substantiate this figure.

4.15.7 In 1988 each UK citizen with some natural teeth, aged 16 and over carried 8.4 restorations on average including amalgam and non amalgams (personal communication DoH). This statistic is reducing primarily due to improved dental hygiene. Therefore assuming there is a higher incidence of amalgam restorations in the older population only, we have assumed a figure of 6 amalgam restorations per person.

4.16 UK Dental Mass Balance Estimate for 1995

4.16.1 For the purposes of this mass estimation, we will use a working estimate of 13,420,000 as the total number of amalgam restorations carried out in the UK in 1995. This is derived from the data in Table 4.5;

Table 4.5 - Number of amalgam fillings for the 1995, UK

England and Wales	9,774,763
Scotland	1,364,000
Northern Ireland	500,000
Private	500,000
Armed Forces	111,000
Deciduous (children)	669,000
Other activities	500,000
Total	13,418,763

4.16.2 A mass balance estimate has been prepared to illustrate the magnitude of mercury flux associated with dental health in the UK. The mass balance shown in Table 4.6 is in terms of mercury only.

4.16.3 The conceptual basis of the mass balance estimate is the restoration mercury mass placed, as shown diagrammatically in Figure 4.3.

4.16.4 Due to the uncertainty regarding the mean mass of restorations placed, a mercury mass range is given. The low value assumes a 400 milligram mercury input and the high value a 600 milligram mercury input. The flux diagram (Figure 4.4) is based on the mean estimate.

4.16.5 Conversations with dentists have revealed that up to 25% of the triturated amalgam prepared is wasted. This is a considerable reduction on the 40% loss assumed in previous studies. Of this scrap, 80% (20% of total input) is assumed to be recovered to storage (i.e. clean excess amalgam) and the remaining 20% carved in the mouth (5% of total input) going into the suction system.

4.16.6 67% of restorations are estimated to be replacements for existing fillings. This is on the basis that the maximum restoration life is around 20 years, therefore 2 replacements will be placed during an average person's life.

4.16.7 Mercury is known to leach in small quantities from amalgam restorations. The quantity leached daily will be related to the number and condition of amalgam surfaces present. The inorganic mercury leached will be present in urine and faeces. A range of 4 to 15 µg mercury per head per day has been used in this estimation for urinary mercury excretion and 27 to 150 µg mercury per head per day for faecal mercury excretion. A transient higher mercury concentration could be expected in the days immediately after dental work.

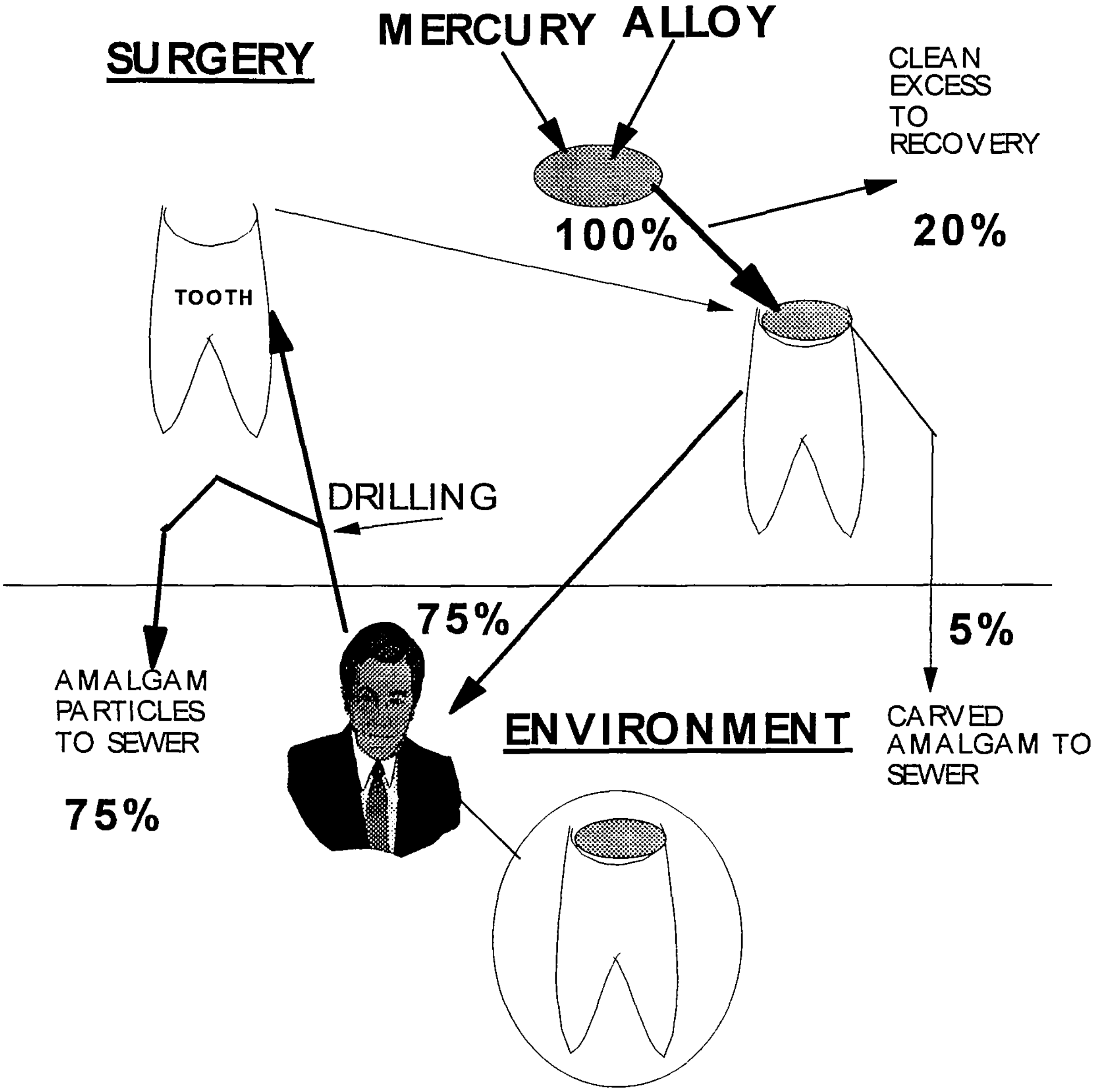


FIGURE 4.3 - CONCEPTUAL BASIS OF MASS BALANCE

4.16.8 The quantity of mercury in extracted teeth passing to clinical waste has been estimated on the basis that 75% of persons having extractions possess an average of six amalgam restorations. 1,940,638 extractions were carried out in England and Wales in 1995 (over 16s only). If the probability of extracted teeth having amalgam restorations is 6 out of 32, then around 364,000 extracted teeth contained amalgam.

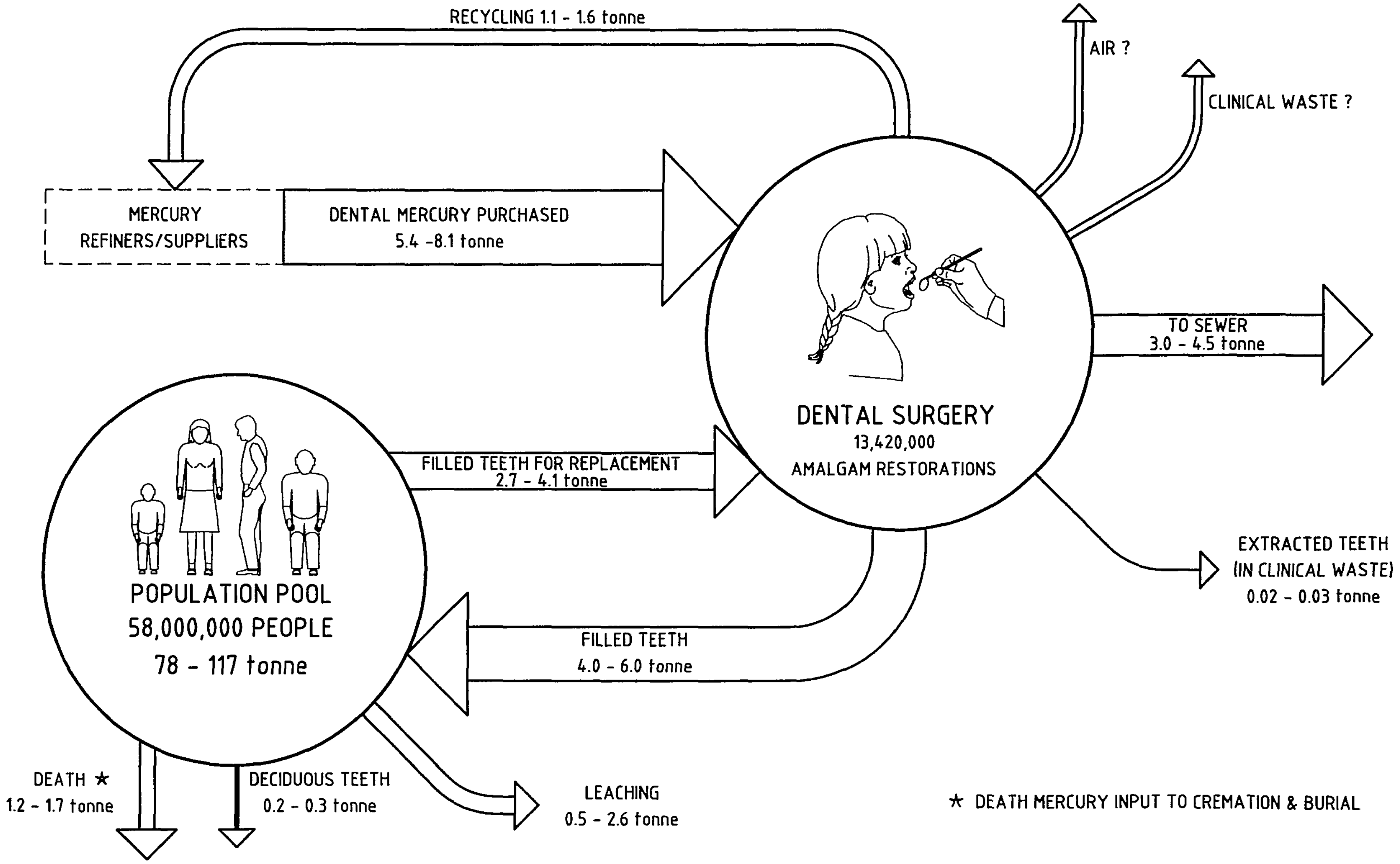
4.16.9 Given that the mercury discharge to sewer from dental surgeries is between 4.45 and 2.97 tonnes per annum and if the number of practising dentists in the UK is 20,000, this gives an annual release per dentist (specific emission factor) to the sewer of;

149 to 223 grams mercury dentist/year
330 to 494 grams amalgam dentist/year

4.16.10 In one amalgam separator company's experience (Metasys), the typical amalgam mass released by one dental chair is one kilogram per year. On this basis the 500 milligram mean filling mercury mass estimate used here could be low. However, if the number of UK dentists performing conservation work is significantly lower than 20,000, and the number of chairs in frequent use for restoration work is around 12,000 then the amalgam release per dentist will increase towards the one kilogram benchmark. Also, the benchmark figure of one kilogram per chair per year is obviously related to the healthcare system and the patient throughput.

Table 4.6 - Dental Mercury Mass Balance for UK - Annual Steady State Analysis for 1995

Mass	Unit number	Mass Estimate Mercury Tonnes/Year		Comment
		High	Low	
Mercury Inputs				
Triple distilled mercury	13,420,000 fillings	8.05	5.37	
Filled teeth for drilling	8,991,400 fillings	4.05	2.70	Assumes 75% of original filling mass retained in teeth & 67% of total fillings performed are full replacements
TOTAL INPUTS		**12.1**	**8.1**	
Surgery Mercury Releases				
Retained in teeth	13,420,000 fillings	6.04	4.03	75% of original amalgam input retained in teeth
Clean excess amalgam	12,420,000 fillings	1.61	1.07	Clean amalgam recycled - 20% of new filling mass
To sewer				
- old amalgam removed	8,991,400 fillings	4.05	2.70	Removed amalgam assumed to be 75% of original mass
- shaping new fillings	13,420,000 fillings	0.40	0.27	5% of new filling mass
RELEASED TO SEWER		**4.45**	**2.97**	
***In vivo* standing crop in Population fillings**	43,500,000 people	117	78.3	58 million population, 25% with no fillings or dentures Average 6 fillings per head
***In vivo* leaching from fillings**				
	43,500,000 people			58 million population, 25% with no fillings or dentures
		0.24	0.06	5 to 15 μg Hg/head/day excreted in urine
		2.38	0.43	27 to 150 μg Hg/head/day excreted in faeces
RELEASED TO SEWER		**2.62**	**0.49**	
Other Mercury Releases				
Extractions to clinical waste	1,940,638 teeth	0.04	0.02	Total extractions assumed = 1.2 x Eng + Wales total. 75% with 6 fillings. % = 6/32 filled teeth out of total.
Death - burial or cremation	638,000 people	1.72	1.15	Assumed death rate 11.0 per 1000, 75% with fillings
Deciduous teeth to landfill	669,000	0.30	0.20	882,180 deciduous fillings in 1989/90 reduced by 25%
TOTAL OTHER RELEASES		**2.06**	**1.37**	



★ DEATH MERCURY INPUT TO CREMATION & BURIAL

FIGURE 4.4 - ANNUAL BULK MERCURY FLUX ASSOCIATED WITH AMALGAM FILLINGS

4.17 Other Survey Comparisons

4.17.1 Four previous studies have addressed dental amalgam use and release in the UK since 1990. The results from this study are compared with previous findings.

Study and estimation year	Mercury mass per filling grams	Filling Number	Mercury discharged to sewer kg	Recycled mercury kg	Specific Emission Annual mercury release to sewer grams/dentist
ERM 1990	1.0	19,000,000	7,000	10,500)	-
WS Atkins -1990	1.0	17,000,000	9,900	1,740	619
HMIP -1993	1.25	20,000,000	12,480	7,500	-
WS Atkins low 1993	0.6	16,000,000**	5,304	1,920	265
WS Atkins high 1993	0.8	16,000,000**	7,072	2,560	354

** assumed a 15% reduction in number of fillings since 1989/90.

4.17.2 This table shows a progressive decline in the mass of mercury reaching the environment as waste amalgam reflecting the decreasing number of amalgam restorations placed since 1990.

4.18 Feasibility, Cost and Benefit of Amalgam Reduction Measures

4.18.1 The situation regarding use of dental amalgam in the UK is complex and involves professional, environmental, safety, health and cost aspects. The implications of altering the supply, fitting and other overheads associated with dental treatment in the UK are extremely intricate and would need to be the subject of an informed investigation for firm conclusions to be drawn.

4.18.2 In order to provide a debating framework, we have assessed the cost and environmental benefits of reducing amalgam use in a simplistic manner by expanding currently available information.

4.18.3 The only means of significantly reducing the mercury load in the sewer system is to regulate releases from dental surgeries. Mercury leaching from the population's amalgam restorations is an intractable release in the short and medium term.

4.18.4 There are three potential strategies available to reduce dental surgery emissions of amalgam mercury, plus the no "action" condition when the quantity of dental amalgam consumption and release declines in proportion to improving dental hygiene.

The UK could;

- ban dental amalgam restorations; either totally or partially in defined situations such as deciduous teeth. The legislative vehicle for such an action is unclear;
- make the fitting of amalgam separators or equivalent mandatory on sewer discharges from dental surgeries;
- use economic instruments or similar to encourage the use of composite materials instead of amalgam.

4.18.5 There are European precedents for some of these initiatives;

- Sweden has introduced some restrictions on use of amalgam fillings for deciduous teeth. It is important to note that the restrictions are on environmental rather than safety grounds (Gordon et al. 1993);
- Germany, Sweden, Switzerland, Denmark have made, and Holland and Norway intend to make, the fitting of amalgam separators mandatory at dental clinics. A minimum amalgam removal efficiency of 95% is usually specified. Consequently separators are of an advanced design using centrifugation technology reliably achieving up to 99% removal efficiency. Recovered amalgam is returned for disposal or recovery using an organised postal scheme involving prepayment and returned credits.

4.18.6 Currently amalgam restorations are the professions' preferred option when compared to bulk use of composite restoration materials for a number of reasons. Amalgam as a restoration material;

- is a cheaper material than composite alternatives;
- is quicker and easier to fit;
- lasts longer than composite compounds; up to 20 years for amalgam compared to 5 years for composite materials;
- can be fitted into most cavities, whereas composite materials may not be suitable for all situations.

Both amalgam and composite restoration materials may have toxicological implications from the substances used.

4.18.7 There are two factors in favour of non-amalgam restorations;

- public awareness of the potential toxic effects of mercury is increasing and therefore could be instrumental in forcing policy changes. Media interest is increasing and the BDA has published guidance to dentists for answering questions from the public on amalgam safety aspects (Gordon et al. 1993, Eley et al. 1993).
- the commercial pressures to develop alternatives to amalgam will intensify accelerating development of new composite materials.

4.19 Potential Options and their Impact on Mercury Release

4.19.1 Option 1 - Prohibition of Amalgam Fillings (phased in over a suitable period)

- Ban all amalgam fillings and fit composite materials when appropriate

  Immediate release to sewer reduction from no new amalgam fillings up to 0.4 tonnes mercury per year.

  Ongoing sewer release from replacing existing fillings up to 4.05 tonnes mercury per year for around the next 20 years until amalgam fillings are no longer significantly present in population.

- Ban amalgam fillings in deciduous teeth only.

  This is equivalent to around 670,000 fillings per year making a mercury release to sewer reduction of up to 0.02 tonnes per year feasible.

Cost Aspects

Information from several Nordic countries and the USA show that for large amalgam fillings, composite materials are between 1.25 and 3 times the cost of amalgam, and gold fillings between 5 and 15 times the cost (Mjor 1992). For small single surface fillings, the cost multiples are less corresponding to between 1.15 and 1.8 for composites or 4.1 to 7.3 for gold. On a longevity basis, composite and gold fillings cost between 4 and 8 times more than amalgam.

We conclude that banning amalgam fillings will increase dental costs as non-amalgam composite materials are more expensive to supply and fit, and do not last as long. The health and safety hazards of handling and installing amalgam materials would be eliminated from clinics. Surgery releases to sewer continue until amalgam restorations eliminated from population. Mercury leaching would reduce in relation to the number of restorations in the population.

4.19.2 Option 2 - Fit amalgam separators to all dental clinics within say a 5 year period and continue with amalgam restorations

Assuming 100% separator fitment is achieved and 95% amalgam removal efficiency is the minimum specification, then after 5 years up to 4.45 x 0.95 = 4.23 tonnes mercury will be prevented from reaching the sewer and can be recycled.

Cost Aspects

Amalgam separators are supplied as integral components of new surgery furniture or are available as stand-alone retrofit units. Budgetary costs for these units in the UK are £1,500 to £3,000 respectively.

On the basis of 20,000 practising dentists in the UK, the budget cost of fitting stand-alone amalgam separators for each dentist is of the order of £40 million spread over the induction period for compliance. However, this cost estimate can be reduced substantially by fitting common separators treating surgery waste for a number of dentists at larger clinics and hospitals. No accurate figures are available for the total number of UK clinics, but assuming 12,000 NHS clinics plus 2,000 private practices, this makes a cost of around £28 million a working figure. Commercial competitive pressures could reduce the cost of separators supplied in large numbers.

The advantages of fitting efficient amalgam separators are rapid large scale mercury release reductions, no change to dental operating practice or filling supply costs and mercury recovery for reuse; the disadvantages are the capital cost and health and safety considerations from continuing amalgam use. The mercury burden leached from amalgam restorations reduces only slightly as the total number of fillings in the population declines according to improvements in dental hygiene.

4.19.3 Option 3 - Influence the development and fitting of alternative materials by economic or directives from Department of Health.

The cost implications of this option are uncertain, however the impact on mercury discharge would be of a similar pattern to a total ban.

4.20 Conclusions

4.20.1 In the absence of widespread abatement or changes in dental practice, waste dental amalgam release is the next largest mass mercury release after the chlor-alkali industry. This is despite a progressive reduction in the number of restorations placed year on year.

4.20.2 The estimated mercury contribution to waste water from dental activities and filling leaching lies in the range 3.5 to 7.1 tonnes in 1995.

4.20.3 Mercury leached from amalgam restorations in the population is a significant release to the sewerage system which will not be reduced by fitting amalgam separators to dental surgeries.

4.20.4 Dental amalgam waste impacts on all environmental compartments and is arguably the largest non-industrial mercury discharge received at most municipal waste water treatment works. Although amalgam use is expected to decrease slowly with improving dental hygiene and availability of alternative materials, there are no foreseeable large scale consumption reductions expected in the absence of regulatory action.

4.20.5 As in previous studies, the 1995 mass balance presented is based on a mixture of data and assumptions. Until further information to refine the assumptions is obtained, then the mass balance remains speculative only.

Particular assumptions requiring more study are:

- the average amalgam restoration mass at preparation;
- how many restorations are replacements;
- the mean quantity of newly mixed amalgam wasted;
- the mean amount of amalgam retained in teeth.

A newly commissioned DoE survey of dentists should provide more detail on these aspects in 1997.

4.20.6 Selective banning of amalgam restorations will reduce releases to land and water by a small amount in the short term, but elimination of mercury from the environment concords with current philosophy under IPC and from the EU. However, alternative restoration materials will be more expensive and significant mercury releases would continue in the medium term.

4.20.7 Making mechanical amalgam separators or equivalent mandatory will achieve immediate reductions in releases to land and water, but other releases during amalgam material production and from the dental clinic will continue e.g. to clinical waste. Fitting amalgam separators is a once only capital cost with minor operating costs, however how the cost of fitting separators would be financed is not clear given that most dentists are private businesses. Fitting amalgam separators will not reduce mercury leaching from fillings in the population.

4.20.8 Installation of amalgam separators is mandatory in at least five European countries.

4.20.9 From our investigations, we conclude that there is considerable uncertainty about the chemistry of amalgam in dental pipelines and in the waste water environment. Mercury could be released from the amalgam to form a number of reactive species, alternatively it could remain in a relatively benign form ultimately reaching land as sewage sludge, or landfill. Likewise the quantities of mercury leaching from amalgam restorations and its fate in waste water is not clear.

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5. UK CHEMICAL INDUSTRY

5.1 Mercury

Overview of Uses and Discharges

5.1.1 The use of mercury in the UK chemical industry is dominated by the chlor-alkali industry. Although, historically, mercury has been used in the manufacture of agrochemicals, pharmaceuticals, paints and catalysts, there are believed to be no significant manufacturing facilities for these products currently operating within the UK.

5.1.2 There are two other significant chemical manufacturing processes currently operating in the UK which result in mercury discharges to water, ie:

- titanium dioxide manufacture;
- phosphoric acid processing.

5.1.3 The current level of mercury discharges to water from the UK chemical industry is summarised in Table 5.1.

Table 5.1 Estimate of Mercury Discharge to surface waters by Chemical Industry Sector in 1995

Industry Sector	Mercury Discharge kg/year
Chlor-Alkali	290*
Titanium Dioxide	8**
Phosphoric Acid	7
Total	305

* Data from IPC Public Registers
** ERM 1996

Chlor-Alkali Processes

5.1.4 The chlor-alkali industry produces chlorine and caustic soda for a wide range of industrial uses, and in the UK the predominant production process is the mercury cell - approximately 72% of the total UK capacity of 1.2 million tonnes of chlorine per annum is based on this technology. Table 5.2 summaries the capacity and technology utilised by the current UK chlor-alkali processes.

Table 5.2 UK Chlor-Alkali Production Facilities (1996)

Facility	Design Capacity (tonnes Cl_2/year)	Technology
Associated Octel	40,000	Membrane cells
Hays Chemicals	89,000	Mercury cells
ICI Runcorn	737,000	Mercury cells
	30,000	Membrane cells (used to manufacture potassium hydroxide solutions)
ICI Wilton	170,000	Diaphragm cells
ICI Lostock	90,000	Diaphragm cells (75no.) and membrane cells (24no.)
Rhône-Poulenc Staveley	28,000	Mercury cells
Total	1,184,000	Mercury cell capacity = 854,000 tonnes Cl_2/year

Data from IPC public registers except ICI Wilton (personal communication ICI chemicals).

5.1.5 In addition to the processes summarised above it should be noted that Associated Octel operates a process to manufacture sodium metal by the electrolysis of molten sodium chloride. The process also generates up to 35,000 tonnes/year of chlorine as a co-product.

5.1.6 Mercury cells consume mercury by releasing the metal by different routes; in the caustic soda product, vented to air, in liquid effluent, in solid waste to landfill or as unaccounted for losses usually attributed to accumulation within the process units. Most mercury is released in solid waste and in the unaccounted for fraction.

5.1.7 The application of the three main chlorine production technologies is discussed below.

a) Mercury Cell

The mercury cell consists of two parts: the electrolyser and the decomposer. The electrolyser is a long trough, slightly inclined to allow mercury to flow in a thin layer along the bottom forming the cathode. Titanium anode plates are suspended above the mercury, and purified brine (at 25% $^{w}/_{w}$) is fed into the cell and electrolysed. The main anode reaction is:

$$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$$

The chlorine gas is piped away from the top of the cell. At the mercury cathode, sodium ions are discharged to form sodium metal, which amalgamates with the mercury and flows with it from the cell.

The amalgam flows into the decomposer which is a packed bed steel reactor containing graphite surfaces. Deionized water is added which reacts with the sodium in the amalgam on the graphite surfaces, and caustic soda and hydrogen gas are produced. The mercury is washed with water to remove caustic, and then returned to the electrolyser:

$$2Na(Hg) + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$$

The mercury cell produces high grade caustic of concentration 50% w/w which is then filtered to remove mercury (Barnes et al 1987, personal communication ICI).

The major source of mercury-contaminated water is the waste brine from the cell, containing 2-15 g Hg/tonne Cl_2. This is combined with other mercury-contaminated aqueous streams such as wash-down water, waste water from filtering operations, washings from surface spillage, drainage from mercury cell rooms, condensates from hydrogen and chlorine gas cooling etc. In the US, studies have shown that the maximum flow of mercury-contaminated, waste water was 6.3 m^3 per tonne chlorine produced, with an average of 2.1 m^3/tonne (USEPA 1980) .

There are three main techniques currently used in the UK chlor-alkali industry to remove mercury from waste water.

i) Zinc Amalgamation

Liquid effluent is fed into a stirred reaction vessel containing zinc granules which form a solid amalgam with any soluble mercury present. Periodically the solids are removed from the reactor for disposal to landfill.

This technique was utilised by Associated Octel to treat cell hall waste water prior to the replacement of their mercury cells with membrane cells in 1992. The zinc reactors still treat waste water to remove any residual mercury arising from pipework and equipment.

In the period 1993-1995 the quantity of mercury discharged from the zinc treatment plant to the water environment was between 37 - 156 kg/year (IPC public register) .

ii) Sulphide Precipitation

The liquid effluent is adjusted to pH 2.5 to dissolve elemental mercury before the addition of sodium sulphide (in slight excess) which reacts with soluble mercury to precipitate mercuric sulphide. The precipitated solids are removed by filtration and the treated waste water can contain <0.15 mg/litre mercury. Once it is fully loaded the filter is washed with sodium hypochlorite and air agitated. This process oxidises the insoluble mercuric sulphide to soluble mercuric sulphate which can then be recycled to the cell hall. The electrolysis process then recovers elemental mercury.

This technique is currently used by ICI to treat the liquid effluent from the mercury cells at their Runcorn site. In the period 1993 - 1995 the quantity of mercury discharged to the water environment was between 245 - 345 kg/year (0.33 - 0.47 g mercury/tonne Cl_2 mercury cell capacity)(IPC public register) .

(iii) Resin Adsorption

The liquid effluent is acidified (to pH 1.5 - 3.0) and oxidised (typically with sodium hypochlorite) to convert insoluble elemental mercury to a soluble ionic form. Other pre-treatment stages can include:

- chemical addition to reduce residual free chlorine;
- sand filters to remove particulate;
- carbon adsorption beds to remove any remaining traces of chlorine.

The effluent is then passed through an ion exchange resin bed which removes the mercury from the waste water stream. Periodically the resin is regenerated by acid washing. The mercury rich acid stream is then recycled to the cell hall where the electrolysis process reduces the soluble mercuric salt to elemental mercury.

This technique is used by both Hays Chemicals and Rhône-Poulenc Staveley. In the period 1993-1995 the quantity of mercury discharged to the water environment from these sites was between 4.4 - 6.3 kg/year (0.05 - 0.07 g mercury/tonne Cl_2 capacity)(2) and 0.25 - 0.5 kg/year (0.01 - 0.02 g mercury/tonne Cl_2 capacity) respectively.

b) Diaphragm Cell

The diaphragm cell has been used in industry for as long as the mercury cell, and 22% of UK capacity currently uses this technology. Essentially it consists of anode and cathode compartments separated by an asbestos diaphragm. At the anode, chlorine gas is produced by the same reaction as in the mercury cell, and the brine flows through the diaphragm into the cathode compartments where the reaction is:

$$2H_2O + 2e^- \dashrightarrow H_2 + 2OH^-$$

Sodium ions migrate towards the cathode where they combine with the hydroxide ions to form the caustic soda.

One of the disadvantages of this process is the use of asbestos (which has its own environmental and health and safety issues). Also, in comparison to the membrane cells the quality of the caustic soda produced is lower and the overall energy consumption is higher (Eurochlor 1993). The quality of caustic soda is also lower than that produced by mercury cells (USEPA 1980).

c) Membrane Cell

The development of membrane cell technology was part of the drive to eliminate mercury from Japanese industrial activity following the Minimata Bay incident.

Approximately 5% of UK capacity currently uses this technology. The anode and cathode compartments of the cell are separated by a chemically active membrane, such as PTFE modified to contain active sites, which permit sodium ions to pass through but not the passage of chloride and hydroxide ions. The anode reaction producing chlorine gas is the same as described previously, but the sodium ions from the anolyte are selectively transported to the cathode compartment where they combine with the hydroxide ions produced at the cathode to form caustic soda, at a concentration up to 30% w/w.

The main advantages of the membrane cell technology are that it does not require the use of mercury or asbestos. The technology also consumes less energy than mercury or diaphragm cells.

There are some disadvantages associated with membrane technology (personal communication ICI) including;

- any depleted brine discharged as effluent contains significantly higher chlorate levels;
- tail gas fed to an ethylene dichloride reaction could contain sufficient oxygen to create a flammability issue;
- chlorine from membrane cells behaves differently in some respects; for example it retards or prevents some chlorination processes requiring the use of additional initators.

Phosphoric Acid Processing

5.1.8 One site in the UK processes up to 400,000 tonnes/year of imported "green" phosphoric acid to produce 195,000 tonnes/year of phosphoric acid for the manufacture of phosphate fertilisers. Mercury is present as an impurity in the "green" phosphoric acid feed and is therefore contained in the process liquid effluent.

5.1.9 The majority of this effluent is treated (the process IPC authorization currently allows up to 12% of the effluent to be discharged direct to the Irish Sea) to generate a solid waste suitable for disposal to landfill. In 1995 the total mercury discharged to surface water from this process was 7 kilograms (IPC public register).

Titanium Dioxide Manufacture

5.1.10 Titanium dioxide is currently manufactured in the UK by two routes:

a) chloride process, ie oxidation of titanium tetrachloride ($TiCl_4$) which is produced by the chlorination of rutile sand and ilmenite one concentrate. This process is operated by Tioxide at Cleveland and SCM Chemicals at Grimsby.

b) sulphate process, ie. acid decomposition of ilmenite ore concentrate followed by the precipitation of metatinic acid (H_2TiO_3) which is then ignited at 950°C to yield TiO_2. This process is operate by Tioxide and SCM Chemicals, both at Grimsby.

5.1.11 Mercury is present as a trace contaminant in the titanium ores ilmenite and rutile and can be present in sulphuric acid reagent used in the sulphate process.

5.1.12 The chloride process does not lead to significant releases of mercury to surface waters. However, the sulphate process generates large volumes of liquid effluent (500,000 m^3 in 1990) which contain mercury as outlined in Table 5.3 below.

Table 5.3 Mercury Discharges to Water from the Sulphate Process

Manufacturer	Mercury Discharge (kg/year)			
	1990	1991	1992	1993
Tioxide	10	10	5	5
SCM	70	30	14	3
Total	80	40	19	8

Data: ERM 1996

The decrease in mercury discharges between 1990-1993 was mainly due to:

a) substantially reduced use of by-product sulphuric acid from the lead/zinc smelting industry, and

b) increased calcium carbonate neutralisation of acid waste waters to precipitate gypsum.

Mercury Based Chemical Products

5.1.13 Historically mercury was used in a range of chemical products although its use has declined substantially or totally stopped in recent years.

- Agrochemicals

  Agricultural applications of mercury containing compounds have been progressively phased out as a result of the 1979 EU Prohibitions Directive 79/117/EEC which required that plant protection products containing listed active ingredients were not used or marketed. An amendment to the Directive in 1991 withdrew the approval from the last remaining mercury containing products with effect from 31 March 1992. There is therefore no manufacture of mercury containing agrochemicals in the UK.

- Pharmaceuticals

  The major medical uses of mercurials are as diuretics and preoperative antiseptics. The use of these compounds has declined sharply due to toxicity concerns and the development of effective alternatives. There is not believed to be any significant manufacture of these compounds in the UK. However, mercury compounds may be used as preservatives in some medicines.

- Paint

  Phenylmercuric acetate and phenylmercuric oleate were used as bactericides in paint. However a 1989 amendment to the 1979 EU Marketing and Use Directive 79/769/EEC banned the use of mercury in anti-fouling, wood preservation and biocidal preparations. It is believed that there is now no manufacture of mercury containing paint additives in the UK.

- Catalysts

  Mercury compounds are used as catalyst for a number of organic chemicals manufacturing processes. These include the production of urethane foams, vinyl chloride monomers, anthraquinone derivatives for dye stuffs, amines and stannous salts. Information on the amount of mercury currently used and aqueous waste discharged was not available.

5.2 Cadmium

Overview of Uses and Discharges

5.2.1 The only current uses of cadmium in the UK chemical industry are for the manufacture of pigments and PVC stabilisers (Personal communication Cadmium Association). However, in the past the processing of phosphate rock and "green" phosphoric acid for the manufacture of phosphate fertilisers has led to significant discharges of cadmium to surface waters (ENDS 1991).

Table 5.4 Estimate of Cadmium Discharge to Surface Waters by Chemical Industry Sector in 1995

Industry Sector	Cadmium Discharge (kg/year)
Phosphoric Acid	2850
PVC Stabilisers	20
Pigments	6
Total	2876

Phosphoric Acid

5.2.2 Phosphoric acid, for use in the manufacture of phosphate fertilisers, used to be manufactured from both imported phosphate rock and "green" phosphoric acid, both of which contain cadmium as an impurity. However, the use of phosphate rock has now ceased and Albright & Wilson now uses 400,000 tonnes/year "green" acid to produce 195,000 tonnes/year phosphoric acid.

5.2.3 Also, the site liquid effluent treatment facilities, which remove cadmium from wastewater and produce a solid waste for landfill disposal, have been expanded in recent years. As a result of these two significant changes discharges of cadmium from the process to surface waters have been substantially reduced. The cadmium discharge consent has been reduced from 40,000 kg/year in 1990 to 5550 kg/year in 1995. The actual cadmium discharge to surface waters in 1995 was 2850 kg/year (IPC public register).

PVC Stabilisers

5.2.4 Cadmium based PVC stabilisers are still used for some applications although they are increasingly under pressure from alternative compounds, particularly barium/lead stabilisers. There is currently believed to be only one company manufacturing cadmium based stabilisers in the UK, ie. Akcros Chemicals. In 1995 Akcros chemicals manufactured approximately 500 tonnes of cadmium stabilisers, using approximately 50 tonnes of cadmium oxide.

5.2.5 Liquid effluent from the manufacturing process is treated with sodium hydroxide to precipitate cadmium oxide/hydroxide. The solids are allowed to settle before the liquor is decanted to drain via a filter. The precipitated and filtered cadmium bearing solids are sent for landfill disposal. In 1995 the final effluent discharge to sewer contained a total of 20 kilograms cadmium (IPC public register).

Pigments

5.2.6 Cadmium is used to manufacture a range of red and yellow pigments. The red pigments are based on a cadmium-sulphur-selenium matrix. The yellow pigments are based on a cadmium-zinc-sulphur matrix.

5.2.7 The manufacture of cadmium pigments involves the following main stages:

a) oxidation of cadmium metal in air (@800°C) to produce cadmium oxide;
b) addition of water and sulphuric acid to produce a cadmium sulphate solution;
c) addition of a "reaction" solution (eg. sodium sulphide, sodium carbonate,etc) to precipitate the required cadmium pigment;
d) filtration, drying and calcination (to produce the desired pigment shade);
e) slurry up in water and then drying, milling, blending, sieving to produce the final pigment product.

5.2.8 There are currently believed to be two manufacturers of cadmium pigments in the UK (Personal communication Cadmium Association). One company uses cadmium metal as raw material, whereas the other starts with purchased cadmium sulphate solution.

5.2.9 Both manufacturers treat cadmium bearing liquid effluent with sodium carbonate (at pH 9-9.5) to precipitate cadmium carbonate. The cadmium carbonate is either redissolved in acid producing a cadmium sulphate solution which can be recycled on-site, or is recovered for reuse as metal by a metal refinery.

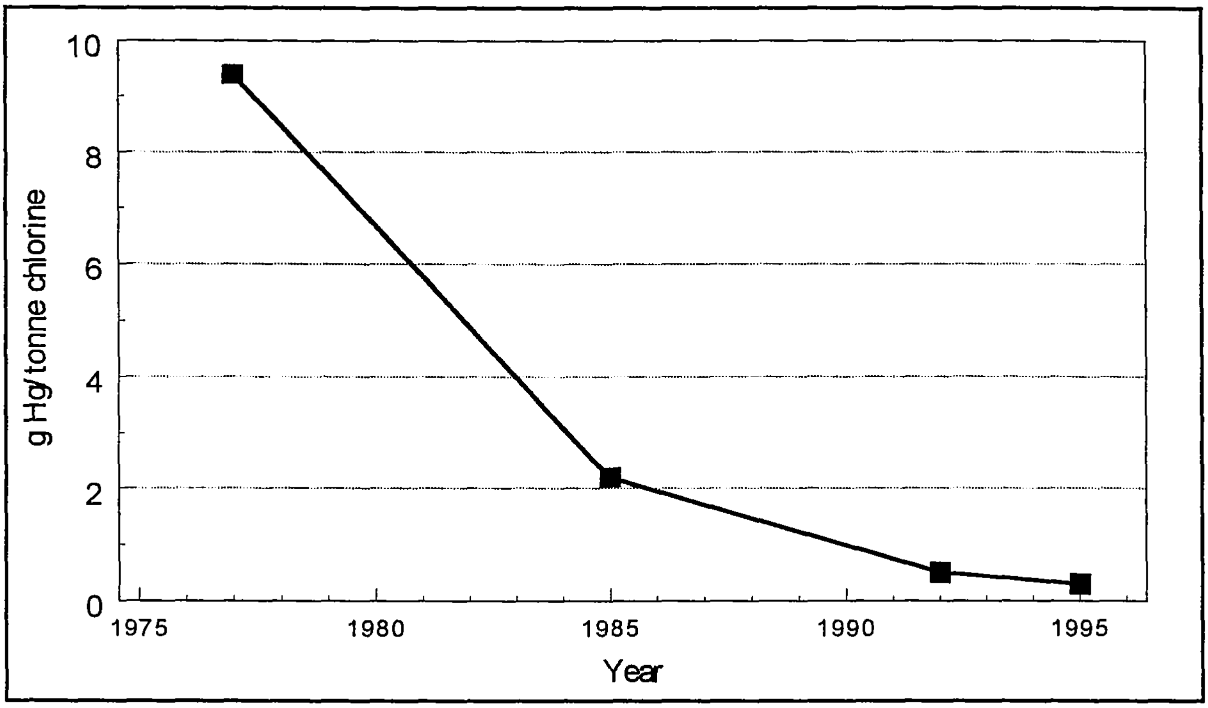
5.2.10 In 1995 the final discharges of treated effluent to surface water contained 6 kilograms of cadmium (IPC public registers).

5.3 Future Trends

Mercury

5.3.1 The release of mercury to surface waters from the UK Chemical Industry is dominated by the chlor-alkali industry sector. It is worth noting at this point that although the sodium hydroxide produced from mercury cells can contain up to 1 gram mercury/tonne (100%) sodium hydroxide, production information indicates that the actual level is typically less than 0.1 g mercury/tonne (Personal communication ICI). Thus, UK sodium hydroxide production will contain approximately 100 kg/year mercury, a proportion of which will enter surface waters through use.

5.3.2 In the last 10-15 years mercury discharges to surface waters throughout the European Chlor-alkali industry (including the UK) have decreased significantly (see Figure 5.1).



(Note: 1995 data is specifically for UK industry based on IPC monitoring returns)

Figure 5.1 Discharges of Mercury to Surface Waters from UK Chlor-Alkali Industry

5.3.3 These reductions have been generated as a result of industry responding to the growing awareness of mercury as a global environmental issue, the former NRA regulation of effluent discharges and water quality and in response to the 1982 EU Controls on Mercury Emissions from Chlor-Alkali Plant Directive 82/176/EEC.

5.3.4 More recently the PARCOM resolution, which followed the third North Sea Conference in the Netherlands in 1990 recommended the complete phase out of mercury cell technology in Europe by 2010 (ENDS 1995).

5.3.5 The European chlor-alkali industry is concerned by what it regards as the excessive cost of converting from mercury cell to membrane technology before the end of the normal working life of the mercury cells (Eurochlor 1993); for example ICI has estimated the cost of converting its Runcorn site to membrane technology at £300 million (IPC public register).

5.3.6 EuroChlor will be proposing a reduction in mercury releases in air, water and land to 1.9 g/tonne chlorine capacity by 2004 (Personal communication ICI).

5.3.7 EuroChlor believes that the 2010 deadline for the replacement of mercury cells will then be unnecessary as the remaining mercury emissions will be insignificant (Personal communication Hays Chemicals). In general, the UK chlor-alkali industry supports the EuroChlor position.

5.3.8 Hays Chemicals apparently intends to convert from mercury cells to membrane technology by 2010 (IPC public register), but this may well be because the mercury cells will reach the end of their working life by this date. It is generally accepted by the chlor-alkali industry that any new or replacement chlorine capacity will use membrane cell technology.

5.3.9 EuroChlor predicts a growth in the demand for chlorine in the order of 2% per annum over the next few years (Personal communication ICI). Some markets are declining, but other major markets are growing strongly, eg. PVC and titanium dioxide. There is believed to be only limited spare production capacity in the UK chlor-alkali industry and thus a sustained, significant growth in the demand for chlorine will require new production capacity. As discussed above any new facilities will use membrane cell technology.

Cadmium

5.3.10 The major release of cadmium to surface waters from the UK Chemical industry is from the processing of “green” phosphoric acid. This process has already reduced its cadmium discharges to surface waters substantially in the last 5 years. Reductions in the percentage of liquid effluent that is allowed to be discharged to the Irish Sea without treatment and optimisation of the operation of a recently installed effluent treatment plant may reduce these discharges further in the future.

5.3.11 The use of cadmium in the chemical industry has generally declined in recent years. The Cadmium Association estimates that the percentage of total global cadmium consumption by the chemical industry has declined from 15% in 1991 to 10% in 1996. The most significant reduction has been in Europe as a result of the restrictions introduced by a 1991 amendment to the 1979 EU Marketing and Use Directive 79/769/EEC.

5.3.12 The market for cadmium PVC stabilisers seems to be gradually declining as a result of competition from alternative compounds, particularly barium-lead compounds. The market for cadmium pigments seems to be fairly stable at its current level.

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6. MERCURY AND CADMIUM IN COAL COMBUSTION

6.1 Introduction

6.1.1 Mercury and cadmium exist as naturally occurring trace metals in all coals. Although present in very small quantities, the sheer volume of coal consumed in the UK means that coal combustion is one of the major emission sources for these substances.

6.1.2 This section introduces literature estimates for the annual total emissions of mercury and cadmium in the UK. We find that these estimates are quite uncertain; because of coal variability, a lack of published information and analytical difficulties. We discuss the efficacy of abatement technologies with reference to the physical properties of mercury and cadmium, before introducing current coal cleaning issues. We conclude with a brief discussion of the future of mercury and cadmium emissions from coal combustion in the UK.

6.2 Overview

6.2.1 Although cadmium is more abundant in coal than mercury, the majority of the literature on this area focuses on the latter, mainly because of its volatility and the consequent difficulty of capture. For this reason, not all estimates or statements regarding mercury can be made for cadmium.

6.2.2 Several good recent literature reviews and reports on this area exist (Sloss 1992, 1995 and White 1996) and this section draws significantly from them.

6.2.3 Coal contains widely variable trace amounts of a large number of heavy metals, including mercury and cadmium. Concentrations vary from area to area and seam to seam, and emission factors are known to be unreliable. In addition, techniques for measuring actual emissions of mercury from large combustion systems are still being developed. The variable speciation of mercury in flue gases is a major contributory factor to this problem.

6.2.4 In 1995, the UK consumed 77 million tonnes of coal, 15 million of which were imported. Figure 5, derived from DTI statistics, shows that UK coal consumption has fallen on average 6½% per year since 1990, when 108.5 million tonnes were used. Domestic coal production has apparently stabilised at around 50 million tonnes per year (DTI 1996), though imported coals typically contain lower levels of mercury and cadmium (Swaine et al. 1995).

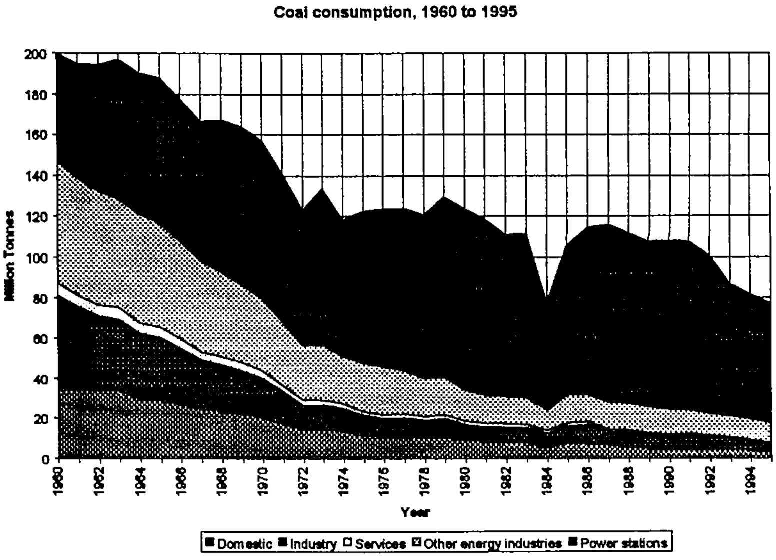


Figure 5 - Coal Consumption in the UK since 1990

6.2.5 The same year, the DoE used emission factors (of around 0.23 mg/kg) to estimate that 18.5 tonnes of mercury were released annually as a result of coal combustion (ERM 1996). This corresponded to 45% of UK mercury releases from fuel combustion. Using emission factors developed by Sloss (drawing on data from many authors worldwide) for cadmium in coals, at least 40 tonnes are likely to have been mobilised.

6.2.6 The overall degree to which mercury and cadmium from coal are subsequently distributed between environmental media is unclear, though substantial (if widely variable) data exists on the efficacy of their capture from flue gases in power stations. In 1995, 78% of all coal consumed in the UK was combusted in power stations. Therefore, although coal preparation techniques would be inherently preferable, there is considerable theoretical scope for metal emission reduction through end-of-pipe technology in power stations. It must be noted that uncontrolled coal cleaning discharges will release mercury in aqueous streams.

6.3 Efficacy of Abatement Technologies

6.3.1 Section 10 discusses in detail the behaviour of mercury and cadmium during combustion processes. This section applies the principles raised specifically to coal combustion air pollution abatement technologies.

6.3.2 During coal combustion, both the mercury and cadmium vaporise, but the cadmium cools sufficiently in the flue gases to precipitate onto the fly ash (Meij 1989). Often 98% of the cadmium will collect in this way, concentrating on the smaller particles (1-5 microns) due to the large surface area / volume ratio (Chadwick 1987). The volatility of mercury and cadmium prevent much remaining with the bottom ash.

6.3.3 The degree of mercury capture from abatement technologies is dependent on flue gas temperature, speciation and residual carbon content. Following coal combustion, less than 10% of the mercury will be present in particulate form, Hg(p), with the rest appearing either as soluble Hg(II) (usually $HgCl_2$) or insoluble, elemental mercury vapour (Hg^o). This speciation is, however, dependent on flue gas temperature and chemistry. For example, high chlorine content is associated with a greater Hg(II) to Hg^0 ratio, and $HgCl_2$ tends to oxidise to HgO above 650°C.

6.3.4 Because of the complexity of the interactions occurring in flue gas systems, the Environment Agency offer no suggestions to Integrated Pollution Control (IPC) inspectors as to the achievable concentrations of metals in flue exhausts from large combustion processes. The revised Guidance Note on these processes states only that: "Releases of metals and metalloids, except volatile metals such as mercury, will be reduced significantly by control of particulate emission levels". In the following sections, we present summaries of how each of the major gas cleaning systems employed in the UK are thought to perform in this respect.

6.4 Particulate Control Systems: Bag Filters, Cyclones and Electrostatic Precipitators (ESPs)

6.4.1 Particulate control devices generally collect greater than the expected maximum of 10% of mercury in particulate form because of the chemical adsorption effect of residual carbon in fly ash. Residual carbon in fly ash is often associated with inefficient combustion and therefore is normally minimised in power station boiler operation, but if present in large amounts can remove large quantities (50-60%) of mercury. Similar improvements can be achieved by lowering the flue gas temperature before the precipitator or filter to facilitate condensation.

6.4.2 'Cold side' ESPs (≅ 140°C) have been shown to remove around 30% of the mercury from flue gas, compared with around 2% in hot side ESPs (≅350°C) in the same plant (Yokoyama 1991). It is unclear whether bag filters out-perform ESPs in this regard. Virtually all large scale coal combustion plants in the UK have hot-side ESPs, and very few have bag filters. Cyclones have a low capture rate for mercury, due to their relative inefficiency at collecting fine particles.

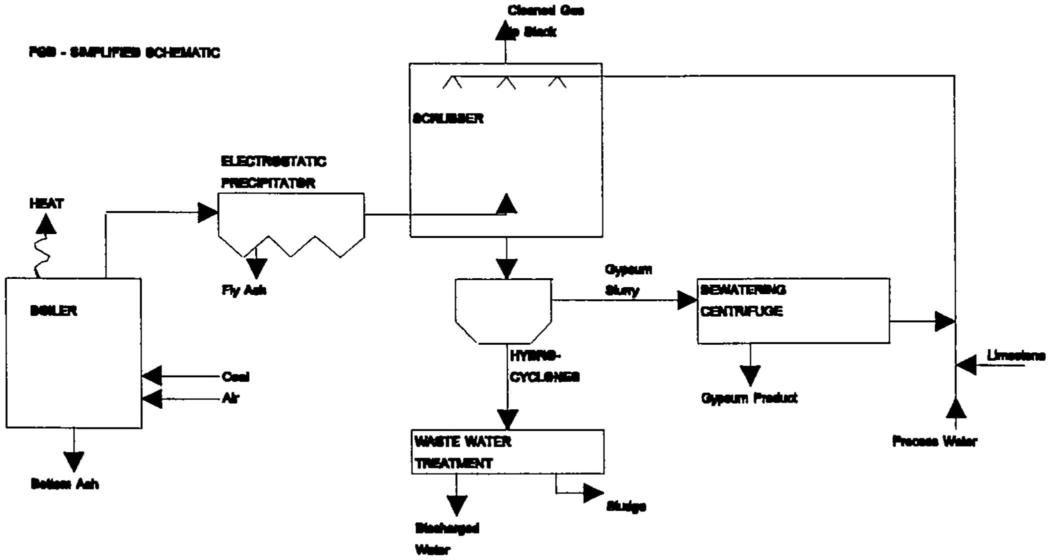
6.4.3 Mass balances show that most (~95%) of the cadmium is removed by standard particulate control equipment, as it has condensed on the fly ash. This fly ash can pose a difficult disposal problem, as under some circumstances, cadmium is readily leached from it. Cadmium has been identified as one of the more mobile trace elements when fly ash is ponded or landfilled (Fernandez-Turiel et al. 1994).

6.5 Wet Scrubbing

6.5.1 Flue Gas Desulphurisation (FGD) systems are designed to scrub SO_2 from flue gases by washing them through a jet of aqueous calcium carbonate (limestone), which reacts to form a calcium sulphate (gypsum) precipitate. In addition to removing soluble metal species, the cold spray also helps to condense vaporised ones.

6.5.2 There are presently two FGD systems in the UK: one plant is operated by PowerGen at Ratcliffe power station, and can produce around 500,000 tonnes of gypsum per year, and a larger plant owned by National Power at the Drax power station in South Yorkshire, which can produce one million tonnes gypsum per year when operating at full capacity. Both these plants have wet limestone injection systems as shown in Figure 6.2.

Figure 6.2 - Simplified Schematic of a Typical Wet FGD System



6.5.3 Both the coal and the limestone are potential input streams of heavy metals, though we have been unable to find British data on this in the literature. The waste streams with a potential for mercury and/or cadmium contamination are shown in Table 6.1, along with their likely metal loads.

Table 6.1 - Fates of Mercury and Cadmium in Combustion Process with FGD

	Cadmium %	Mercury %
Boiler Bottom Ash	Trace	Trace
ESP Fly Ash	95	10
FGD 'Cleaned' Gas	0	63
Gypsum	1	2.7
Waste Water Treatment Plant (WWTP) Sludge	3.9	18
WWTP Liquid Discharge	0.1	6.3

6.5.4 Of the small quantity of cadmium that passes through the particulate capture units, the quantity subsequently escaping from the scrubber stack varies up to 90% (Yokoyama 1991). This wide range is directly related to process conditions, in that the scrubber is very effective at removing cadmium condensed onto particulate, but less effective with the vaporised form. It is likely that the wastewater treatment plant (WWTP) sludge is relatively rich in cadmium. A study on a German power station treating 600,000 m^3/h of flue gas showed that of the 0.86g/h of cadmium entering the FGD system (of which 98% was from the lime!), almost none left in the flue gas, 78% ultimately reached the WWTP sludge, 20% the gypsum and 2% the cleaned water.

6.5.5 In a study of the Studstrup and Voitsberg power stations, the amount of mercury removed in the fly ash is in the region of 30-50%. This is higher than in many other studies which typically quote 0-10% removal, the wide variance due to differing operational conditions (eg flue temperature, coal quality). The subsequent mercury release from the scrubber is around 50-90%, despite the drop in gas temperature to 50 - 60°C. As with cadmium, mercury is not tested for in gypsum for wallboard manufacture, but it is reported that of the 8.77g/h of mercury entering a German FGD plant, 70% was released from the scrubber stack, 20% was found in the sludge, 7% the cleaned water and only 3% the gypsum.

6.5.6 The revised Guidance Note on large combustion processes (HMIP 1995) states that for combustion processes over 50 MW_{th}, IPC inspectors should now set an annual mass water emission limit for mercury and cadmium. The achievable releases to water they suggest are 0.005 mg/l for mercury and 0.01 mg/l for cadmium. A footnote in the document states that a 70% reduction in these substances can be achieved by on-site precipitation and filtration, and subsequent sewerage treatment will clean the water to below the limits of detection (i.e. <0.0001 mg/l).

6.5.7 The gypsum by-product is used commercially in the manufacture of plasterboard and related products. This is likely to delay the dumping of any cadmium or mercury present to landfill for between fifty and a hundred years. At Drax, sub-specification material is disposed of with WWTP sludge under several layers of rolled pulverised fuel ash (PFA - fly ash), which has a permeability in the order of that of clay (Personal communication WS Atkins). Water penetrates this layer over an extremely extended time scale.

6.6 DENOX Systems and Specific Mercury Removal Technologies

6.6.1 Selective Catalytic Reduction (SCR) systems for NO_x removal, when situated upstream of an FGD unit, appear to aid mercury removal there by oxidising Hg^0 species to Hg(II). Between 90-95% of the mercury passing through a high dust SCR was as $HgCl_2$ (Gutberlet et al.). Of this, 35% was subsequently removed in the prescrubber of a wet FGD, and the majority of the rest was removed in the absorber stage of the scrubber. There are currently no UK power stations with SCR equipment, and its retrofitting to existing plant would be difficult due to the configuration of UK boilers.

6.6.2 Much work is currently underway to develop end-of-pipe technologies that specifically remove mercury. Most of this centres around the use of activated carbon, for which impressive mercury removal rates have been achieved. Chemical imgregnation of activated carbon has been shown to enhance this effect. However, the issue of the disposal of mercury trapped in activated carbon has still to be addressed, as do many other technical problems with the injection systems themselves.

6.7 Coal Cleaning and Processing Technologies

6.7.1 The main types of coal cleaning techniques are physical, chemical and biological. Physical cleaning techniques are in widespread use, but only a small number of chemical or biological techniques have progressed to pilot scale, despite the vastly improved cleaning potential.

6.7.2 There is insufficient data to assess accurately coal cleaning's efficacy for mercury removal from coal. However, since mercury and cadmium are reported as being associated with pyrite or other sulphide minerals, it follows that attempts to remove sulphurous minerals may also be successful in removing a significant proportion of any mercury and cadmium present.

6.7.3 UK coal is higher in ash and sulphur than in many other countries. White suggests that the reduction in sulphur and ash prior to combustion appears to be one of the more practicable approaches for the effective removal of part of the sulphur content of coal, and recommends that coal preparation procedures be reviewed to assess whether recent developments in wash plant technology would be cost effective to implement. This, he suggests, would have implications for mercury emissions.

6.7.4 Simple gravity separation of coarse size fractions can be moderately effective at removing trace metals associated with the mineral phases present in coal (Boron et al. 1990). Mercury removal is highly variable (0-61% removal efficiency, mean 27%) for a variety of bituminous US coals. The removal efficiency of mercury apparently depends on the mineral association and the nature of the coal.

6.7.5 Physical coal cleaning techniques are employed primarily to meet specifications e.g ash content, and raise the calorific value of the coal by removing mineral matter. Any corresponding heavy metal removal has been, until recently, incidental. Most coal imported to the UK has been pre-cleaned at source, though it has been pointed out that out that smaller size fractions of British-mined coal have often escaped washing because of historical trade agreements between the coal and utility industries.

6.7.6 The waste material from cleaning operations is presently sent to landfill. Most coal preparation techniques are performed with closed-loop liquid processes designed to prevent liquid disposal.

6.8 The Future of Mercury and Cadmium Emissions from Coal Combustion in the United Kingdom

6.8.1 In his influential discussion of future power generation in the UK, DJ White addresses many issues of relevance to mercury and cadmium from coal combustion (White 1996 a).

6.8.2 Of prime significance will be the actual extent of coal use in the medium to long term. White notes that there is presently much inter-fuel competition, and gas has already displaced much coal, a process which is likely to continue. The medium to long term demand for coal will depend on the availability and price of gas, the uncertainty of which is a key problem for power utility investment strategists.

6.8.3 The other main issue is the prospect of more efficient coal utilisation made possible by Clean Coal Technologies (CCTs). The future of coal may lie with Integrated Gasification Combined Cycle (IGCC) technologies, which essentially mirror the efficient, natural gas-powered Combined Cycle Gas Turbines (CCGTs), but with the added initial stages of coal gasification and purification. IGCCs would reduce all forms of air pollutants by both improving energy conversion efficiency (reducing the coal consumed per unit energy delivered) and through gas stripping prior to combustion. Other forms of CCTs are under development, including Ultra-Super Critical Steam technology and Atmospheric and Pressurised Fluidised Bed systems.

6.8.4 At present, the power utilities are cautious about investing in CCTs, and are apparently waiting to judge the performance of demonstration projects, such as the IGCC Buggenum plant in the Netherlands. Fuel price uncertainties may also prevent the power utilities from investing in expensive coal emission controls unless they are either guaranteed cost recovery or forced to do so by regulation. On this subject, White notes that, "FGD and DENOX control systems are capital intensive control systems which, if added to conventional capacity, would elevate the total installed cost to a level now comparable with the cost of IGCC for coal" (White 1996 b).

6.8.5 Very little information is presently available on the potential extent of mercury or cadmium removal from most CCTs, though it has been predicted that advanced physical coal cleaning may have the potential to achieve significant trace element reductions. Reductions in cadmium exceeding 50% have been reported for certain techniques.

6.9 Conclusions

6.9.1 Mercury and cadmium exist as naturally occurring trace metals in all coals. Although present in very small quantities, the sheer volume of coal consumed in the UK means that coal combustion is one of the major emission sources for these substances.

6.9.2 In 1995, the UK consumed 77 million tonnes of coal, from which 18.5 tonnes of mercury is thought to have been released, mostly to air. Mercury recapture is highly dependent on the extent of residual carbon in the flue gas system, as well as its temperature and configuration. There are significant releases in even the most carefully controlled equipment. Over 95% of the cadmium present in the coal, around 40 tonnes in 1995, is likely to have been captured along with power station fly ash, principally by precipitators, and sent to landfill.

6.9.3 There is presently scope for a considerable tightening of coal cleaning practices in the UK. Given the relatively high ash and sulphur content of many British-mined coals, there is reason to believe that such procedural changes would have an important effect on the reduction of mercury emissions to air.

6.9.4 Extensive investment in clean coal technology, such as IGCC plants, is unlikely to come voluntarily from the power utility companies whilst the medium to long term future of coal utilisation per se is in question in the UK. Although the scale of coal combustion is expected to reduce in the foreseeable future, releases will continue to be significant.

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7. MERCURY AND CADMIUM IN LANDFILLS

Introduction

In this section we review the quantities of mercury and cadmium entering UK landfills and their behaviour therein. There is a risk that toxic metals derived from industrial waste materials or discarded domestic products will mobilise into drainage waters (leachate) and proceed to the sea. There is also a risk that volatile metal species could be present in gases produced and liberated by methanogenic landfills.

Metals could be released from landfills in the short-term as leachate produced during the acetogenic and methanogenic phases of the landfill, alternatively they could be released to water when the landfill stabilises in the future when the chemical environment of the landfill could become more oxidising in nature. Leachate analysis from past and present landfills can be assessed now, but the longer term risk of metal release cannot be confirmed (although some research work has and is being carried out on this aspect).

7.1 Landfill

7.1.1 Previously controlled waste disposal was regulated by County Waste Regulation Authorities. The Environment Agency have taken over this responsibility since April 1996. Effluent to controlled waters from landfills are therefore regulated directly by the Environment Agency or to public sewer by the sewerage undertaker.

7.1.2 It is widely known that the deposition of metal bearing wastes or materials contaminated by trace metal concentrations, onto or into the ground creates a risk of the toxic metals becoming mobile and being released to the environment via leachate, drainage or as a gas. Release is possible in the short, medium or long term. However, physical, chemical and biological attenuation mechanisms occur which, by and large, have prevented large scale metal releases.

7.1.3 Landfill is the largest single disposal method for solid waste in the UK with over 8,000 licensed sites (DoE 1992). Wastes deposited are either controlled, or not controlled under the terms of the EPA and allied legislation. Current information on metal contents from various sources and suggested current waste arisings in the UK are summarised in Table 7.1.

Table 7.1 - Mercury and Cadmium Content of Wastes that may be Landfilled

Waste Source	Waste Arising 1990 tonnes x 10^3	Cadmium Content mg/kg	Mercury Content mg/kg	Cadmium Mass tonnes	Mercury Mass tonnes
Controlled Wastes					
Household	20,000	4 - 12	1 - 5	80 - 240	20 - 100
Commercial	15,000	<0.0001	<0.0001	negligible	negligible
Blast Furnace & steel slag	6,000	?	?		6
Power station ash	13,000				13
- bottom ash		0.3 - 1.5	0.01 - 0.7		
- fly ash		0.1 - 3.9	0.04 - 0.7		
Other	50,000	?	?	?	?
Demolition & Construction	32,000	?	?	?	?
Sewage Sludge (dry weight)	1,058*	7.5	3.7	7.9	3.9
Other Wastes					
Agriculture	250,000	?	?	?	?
Mining & Quarrying	108,000	?	?	?	?
Dredging Spoils	22,900*	0.35	0.34	8.1	7.8
Special Waste	2,896*	?	?	-	-

Sources - DoE (1992), DoE (1993) * - 1991 data

7.1.4 Out of approximately 140 million tonnes of controlled waste produced in 1990/91, 90% was landfilled and 10% was incinerated (Report of the Environmental Committee 1991). Some 88% of the municipal solid waste was landfilled. Approximately 70 to 80% of the chemical industry waste was landfilled with some 40% of this waste being disposed of adjacent to industrial premises. Power station ash is typically landfilled in void space or in above ground mounds. Of the remainder of the non-controlled wastes, sewage sludge is disposed of on agricultural land, incinerated, landfilled or dumped at sea (although this practice will stop by 1998); mining and quarrying waste is landfilled in void space or in above ground mounds and agricultural waste is usually disposed of on farm land.

7.1.5 Special wastes can only be disposed into landfill sites licensed for the purpose. Some 70% of special wastes are landfilled. Waste Management Paper 26 defines as special wastes those containing mercury at concentrations exceeding 20 mg/kg inorganic or elemental mercury, or 2 mg/kg organic mercury.

7.1.6 Despite the recent landfill tax and the hierarchy of waste disposal options, landfill represents a convenient disposal option for waste disposal authorities and private industry alike. Until the costs of landfill increases promoting the production of smaller volumes of more concentrated waste, large scale landfill will continue as the preferred disposal method and impede the evolution of a low waste economy.

7.1.7 There are three generic types of landfill in the UK; mono-disposal sites where one homogenous waste is deposited, multi-disposal landfills accepting a wide spectrum of wastes on an indiscriminate basis and co-disposal sites which make use of in situ processes to neutralise or immobilise wastes. Mono-disposal sites are typical of industrial landfills, multi-disposal sites are the most numerous being used for domestic with some industrial wastes and co-disposal sites are used for the disposal of some special wastes.

7.1.8 The ethos of today's landfill practice is engineered containment and treatment of leachate within the landfill as a managed operation. In the past landfill was operated on a dilute and disperse philosophy with often little or no collection and treatment of leachate except attenuation within the deposited waste material. The monitoring and restoration of such sites is likely to be prohibitively expensive, but there could be significant contributions of hazardous substances to ground water from these sites. The remainder of this text refers to engineered containment sites whether below ground or above ground mounds.

7.1.9 Mercury and cadmium bearing materials enter landfills by three main pathways:

- as special waste from industrial sources such as electroplating residues, chlor-alkali slurries;
- as trace materials in controlled waste - this includes batteries, cadmium pigments, coatings and stabilisers in products from domestic or industrial sources;
- as trace contaminants in sewage sludge or combustion ashes.

7.2 Special Wastes

7.2.1 Industrial mercury and cadmium bearing wastes designated as special are consigned to hazardous waste contractors for treatment and disposal in designated sites sometimes in a co-disposal method with domestic waste. These are typically residues from abatement processes or contaminated production materials including spent reagents, catalysts and vessels.

7.2.2 Liquid or slurry wastes are often subjected to chemical treatment to remove metals from solution. Solids or semi-solids arising are dewatered, for example by plate presses and then solidified using a mixture of portland cement and pulverised fuel ash (PFA). This material is then landfilled under controlled conditions and long term monitoring is undertaken. Liquid effluent is subjected to membrane filtration to remove residual heavy metals to parts per billion concentrations. The efficacy of the immobilisation methods in the longer term is debatable.

7.2.3 Special waste landfills are designed and operated to ensure deposited wastes are sterile, stable and subject to minimum water ingress. Leachate analysis from special waste sites indicates that minimal environmental impact has occurred. In 1989 leachate monitoring results from five full scale hazardous waste disposal sites where co-disposal with municipal solid waste had been, or continued to be carried out was reported (DoE Wastes Technical Division 1989). At one site, 48% of the loads deposited consisted of filter cake containing $CaSO_4$ and metal hydroxides. Cadmium concentrations in the leachate varied from <0.01 mg/l (2 sites) to 0.03 mg/l.

We conclude that the regulatory powers regarding licensing and monitoring of special waste landfill appear sufficient, but are under review regarding the EU draft directive at present. The evidence currently available indicates that minimal environmental impact is occurring from managed sites. However, the greatest risks are associated with historical completed sites and with current co-disposal sites where release opportunities, mercury and cadmium are present.

7.3 Co-Disposal Landfills

7.3.1 Co-disposal sites are where industrial wastes and municipal solid waste are indiscriminately deposited. Although this text refers specifically to cadmium and mercury, other toxic metals and organic compounds are typically present in leachate according to the waste materials deposited.

7.3.2 Municipal solid waste landfills are engineered to maximise biodegradation in order to achieve a stable residue in the shortest time. This is achieved by using the deposited waste material as a fixed film bio-reactor of high hydraulic retention time and controlling the water balance. Bacterial activity is similar to the anaerobic sludge digestion system used for sewage sludge stabilisation. The deposited material mass typically undergoes a succession of micro-environmental changes derived from the bacterial activity although time periods and the actual extremes of condition will depend on the chemical characteristics of the waste material and other geophysical factors.

7.3.3 Deposited municipal solid waste heats up due to aerobic bacterial activity reaching 25°C in shallow landfills and up to 50°C in deep landfills.

When all the available and bound oxygen is consumed;

- the Redox potential progressively reduces to between -300 and -500 mV;
- pH decreases to between 5 and 6 due to the activities of acetogenic bacteria;
- interstitial water ionic strength rises due to the mobilisation of inorganic and organic ligands;
- methanogenesis commences resulting in a recovery of pH to around neutral and the production of landfill gas at a relatively constant rate.

7.3.4 In landfills the reactive medium is stationary and the leachate is mobile. Total containment systems use an impermeable barrier installed to prevent leachate escaping and allow the concept of leachate control which has important implications for landfill management. The introduction of a saturated zone within the landfill maximises biological activity and improves the water balance (and increases the possibility of leachate loss). Leachate drained from the deposited waste can be recycled to improve the water balance or alternatively treated for disposal to controlled waters or the foul sewer.

7.3.5 Continually recycling leachate through the deposited waste mass may cause prohibitively high ionic strengths and therefore may not be permitted due to an increased risk of ground water contamination and difficulties in treating leachate for off site disposal.

7.3.6 The high hydraulic retention times associated with deep landfills allow a long contact time for abiotic reactions to occur. Cadmium present as a surface coating or in an impermeable plastic matrix may be stable for many years, even under the aggressive phases of the landfill. Metal release from deposited batteries are discussed separately in a subsequent section.

7.3.7 The fluctuating physical and chemical conditions existing in the life cycle of a typical municipal solid waste landfill site imply that significant releases of toxic metals are possible especially during the aggressive low pH periods prior to methanogenesis.

7.3.8 Heavy metal speciation within the deposited material will vary according to;

pH	most heavy metal solubilities increase with increasing hydrogen ion concentration. Also hydrogen ions participate in dissociation reactions and redox equilibria;
precipitation	many organic and inorganic anions can precipitate metals as sparingly soluble salts. Anions such as sulphide, carbonate and hydroxide have broad precipitating capacities, whereas others such as chloride or sulphate form sparingly soluble salts with only a small number of metals;
complexation	the formation of metal complexes with ligands tends to increase solubility; for example humic acid complexes and phenol increase the solubility of toxic metals;
redox potential	influences metal speciation and behaviour by modifying the metal itself and by the nature of other species in the environment. For example the reduction of sulphate to sulphide is a critical step in precipitating heavy metals.

7.3.9 The landfill environment provides opportunities for the formation of sparingly soluble metallic hydroxides and carbonates (at high pH). The high ionic strength of the interstitial waters provides opportunity for the formation of soluble complexes with organic and inorganic ligands. However, the landfill also provides opportunities for immobilisation of heavy metals *in the* (virtually) insoluble sulphide form.

7.4 Cadmium

7.4.1 In reality there is little evidence for excessive contamination of landfill leachate by cadmium. In a 1992 survey of 100 landfill sites (DoE Wastes Technical Division 1990), 17 sites reported cadmium analyses. Cadmium was detected in leachate from 3 sites only; concentrations reported were 2 µg/l, 20 µg/l and 960 µg/l with the high value being associated with an unnamed site leachate which also contained excessive levels of other toxic metals including nickel, copper and zinc.

7.4.2 In the 1989 DoE study on co-disposal (DoE Wastes Technical Division 1989), cadmium was identified as the least mobile heavy metal. This study clearly identified the complexity of metal-refuse interactions and that attenuation reliably occurs in landfills. Other work reviewed in this study suggested cadmium adsorbed strongly to newspaper, textile and polythene; although this adsorption was reversible, this was only achieved at low pH and from paper and textile.

7.4.3 A study (Reynolds et al. 1993) investigating metals behaviour in landfill environments concluded;

- under acidic conditions, young refuse released less metal than aged refuse;
- metals are held by increased binding strengths in aged wastes suggesting sulphide formation is occurring;
- cadmium was bound as ion exchangeable forms particularly to paper, soil, textiles and plastics;

7.4.4 A 1995 survey reviewed the composition of leachate from domestic wastes in UK landfill sites (DoE Wastes Technical Division 1995). This study concluded cadmium was not present in significant concentrations in landfill leachate. The study survey of 30 UK sites (primarily domestic wastes) found cadmium concentrations ranging from <10 (detection limit) to 30 µg/l with the mean values being 10 µg/l or less. This study also presented leachate data from other workers; 99% of results reported were less than 100 µg/l with most results being in the range <10 to 20 µg/l.

7.5 Mercury

7.5.1 Mercury within a landfill bulk can exist in several forms;

- elemental mercury formed under reducing conditions from mercury chloride complexes (Gould et al 1989); elemental mercury could be present as the metal, or as dissolved mercury (solubility between 10 and 40 µg/l), or as a vapour in the interstitial atmosphere;

- sparingly soluble precipitates such as sulphide, carbonates and hydroxides; co-precipitation with iron has been suggested as an important mechanism (DoE Wastes Technical Division 1993);
- soluble organo-mercury complexes;
- methylated mercury forms which can be soluble or volatile (present in the interstitial gas vapour phase);
- metallic solids deposited within the landfill, such as $HgCl_2$;
- soluble salts which may be adsorbed to other materials within the landfill mass.

7.5.2 There is very little published data available on the fate of mercury in landfills. In the characterisation of 100 UK landfill sites (DoE Wastes Technical Division 1990), no mercury analysis was reported. The 1989 study (DoE Wastes Technical Division) reported that research work regarding the fate of mercury in landfills was extremely limited.

7.5.3 Some lysimeter studies had shown leachate concentrations in the range 20 to 40 µg/l mercury at refuse loadings of 76 to 304 mg/kg; these concentrations are similar to the aqueous solubility of elemental mercury suggesting reduction of mercury compounds to elemental mercury is occurring. At one site, disposal of rejected lamps containing mercury produced up to 2000 mg/kg in the waste; the maximum leachate concentration was 7 µg/l, but gas samples contained up to 0.2 mg/m^3 mercury. Other work showed that mercurous chloride from battery wastes produced leachate concentrations of 1 to 5 µg/l, but 0.1 to 0.7 mg/m^3 mercury was detected in gas samples. Collectively these investigations suggest that precipitation with sulphide occurs, but conversion to inorganic mercury (which may be volatilised into the landfill gas) is also possible when there are high inorganic mercury concentrations present.

7.5.4 A recent survey reviewed the composition of leachate from domestic wastes in UK landfill sites (DoE Wastes Technical Division 1995) and concluded that typically mercury was not present in significant concentrations. A survey of 30 UK sites (primarily domestic wastes) found mercury concentrations exceeding 0.1 µg/l in 30% of samples with a maximum value of 1.0 µg/l. The overall mean was 0.3 µg/l. This study also presented leachate data from other workers; all results reported were less than 10 µg/l with most results being <2.0 µg/l.

Repeated surveys in the UK and overseas have not detected significant concentrations of mercury or cadmium in leachate from domestic landfills. We conclude there is little or no evidence so far to suggest mass mobilisation of these metals will occur. However, as landfill is the primary terrestrial sink for these toxic metals, due diligence and further research are necessary to safeguard the environment.

The trend towards on-site biological leachate treatment will concentrate the majority of metals present as soluble or particulate species into the solid phase (although volatile species will be stripped to atmosphere by aeration devices). The disposal route of these sludge solids should be determined according to their toxic metal content.

7.6 Mercury and Cadmium Releases in Landfill Gas

7.6.1 Elevated temperatures within the biologically active deposited waste body suggests mercury species may be present as vapour in the landfill gas fraction. Also unique to mercury, there is the possibility of biological methyl mercury (mono methyl and dimethyl mercury) formation during the early warm, oxidising phases of the landfill. Methylation is thought to be inhibited by the presence of sulphide.

7.6.2 In the USA, lysimeters operating in the acid forming landfill phase spiked with inorganic mercury concentrations ranging from 20 to 80 mg/kg showed leachate mercury concentrations peaks up to 4,000 µg/l in the first 200 days, followed by relatively consistent concentrations around 20 µg/l (Gould et al 1989). To explain the mercury peaks, the study suggested that either the divalent mercury was present as chloro-mercuric species (mostly $HgCl_2$) with the residual mercuric ions being in equilibrium with low levels of sulphide; alternatively the redox potential in landfills (typical Eh -200 to -400 mv) is sufficient to reduce divalent mercuric salts to elemental mercury.

Elemental mercury would be water soluble in the range 20 to 40 µg/l and the low vapour pressure would favour evaporation into the gas phase which would be released in the landfill gas formed during the early stages of methanogenesis.

7.6.3 Further evidence for mercury vapour in landfill gas is present in Swedish and Finnish studies. In a Finnish sanitary landfill, mercury concentrations in the working air peaked at 14 µg/m^3 (Koch et al. 1990). In a study of 4 Swedish landfills, mercury concentrations varied from 0.010 to 0.024 µg/m^3 (Bergval et al. 1988). These values are much less than reported when mercury wastes were present in high concentration as discussed in a previous section.

7.6.4 In the UK, the published long-term Threshold Limit Values are 25 µg/m^3 for elemental mercury and 10 µg/m^3 for alkyl mercury (HSE 1996). In Sweden, selenium filtration systems are commercially available for removing mercury from landfill gas.

7.6.5 A 1995 German paper reported analysis of volatile metal and metalloid species in landfill gas (Feldmann et al. 1995). Total volatile metal and metalloid content of landfill gas was estimated to be in the range 0.049 to 0.13 µg/m^3.

7.6.6 A 1990 study (ETSU 1990) estimated the total UK landfill gas availability of 1,117 x 10^6 cubic metres per year. If mercury was present in typical landfill gases at concentrations up to 0.130 µg/m^3, this equates to an annual atmospheric release of;

$$1117 \times 10^6 \times 0.13 \times 10^{-6} \text{ grams}$$
$$= 145 \text{ grams of mercury released.}$$

7.6.7 Therefore mercury release from landfills is concluded not to be a significant environmental problem when compared to other industrial releases, provided the gaseous mercury concentrations reported are representative of UK landfills. When inorganic mercury residues are deposited, mercury concentrations in landfill gas may exceed the TLV for occupational exposure.

In conclusion, the case for significant mercury release from landfills is not proven so far. Any gaseous mercury emissions from co-disposal landfills are expected to be below the TLV and thus represent an insignificant emission at present which may decrease as the amount of mercury in municipal solid waste decreases with time. If inorganic mercury residues are present at high concentrations, gaseous mercury concentrations may exceed the TLV for inorganic mercury, and if microbially methylated would be a significant environmental hazard.

Discarded Batteries in Landfill Environments

7.6.8 The potential hazards of land-filling discarded batteries have been under investigation since the early 1970s when the mercury content of discarded primary cells was of particular relevance. Since the 1970s, the mercury content of non-button primary cells has decreased particularly in the last five years, whereas the quantity of nickel cadmium batteries in circulation and ultimately likely to reach landfill has increased dramatically in the last 5 years.

7.6.9 There are two aspects to the release of mercury and cadmium from discarded batteries in the landfill environment;

- rate of metal release from the battery; the time for the battery pack or cell to corrode or deteriorate sufficiently to make available the cell contents;
- the fate of the cell contents within the landfill environment (covered elsewhere).

7.6.10 An early UK study (Jones et al. 1978) considered the degradation of various dry cells under simulated and actual municipal solid waste landfill conditions. All the dry cells except the Ni/Cd cells contained mercury at concentrations in excess of 1% w/w. The main findings were;

- residual battery charge accelerated corrosion of the cell casing; fully charged batteries corroded faster than discharged batteries although this did not apply to Ni/Cd cells which retain a similar voltage;
- batteries corroded faster under aqueous conditions than in a landfill environment; this was attributed to the formation of external electrical circuits by liquids; generally batteries corroded faster under aerobic than anaerobic conditions;
- mercury cells corroded rapidly, in some cases mercury exposure was visible within a 100 day period;
- alkaline and silver-zinc batteries corroded less rapidly, but the zinc cans of zinc carbon batteries corroded rapidly;
- NiCd cells perforated through the positive terminal face although the plastic packing surrounding the cell stack exerted considerable protection;
- under site burial conditions, mercury cells and zinc carbon cells tended to be badly corroded although the nature of the cell packaging exerted protection in the case of lacquering (cathodic protection), alkaline manganese batteries and Ni/Cd batteries were largely intact.

7.6.11 Additional column leaching and accelerated corrosion leachate analysis tests were performed. Cadmium was not detected in any test leachate exceeding 10 µg/l. Mercury concentrations in leachate ranged from 0.81 mg/l for mercury cell tests to less than 10 µg/l for most other batteries.

The implications of this work are that the corrosion rate of batteries in the landfill micro-environment is mainly dependent on the battery exterior protection, the residual battery charge and the water balance. Mercury cells corrode rapidly and elemental mercury may become available to the environment within 100 days, whereas Ni/Cd batteries are more stable and were largely intact after 7 months burial.

7.7 Conclusions

7.7.1 We conclude that in most cases the evidence shows landfill practice is not releasing excessive loads of cadmium or mercury into the environment. Mercury and cadmium concentrations measured in landfill leachate tend to be similar to domestic sewage.

7.7.2 The impending EU directive on the landfill of waste materials is likely to initiate further research work in these areas as the UK is the main advocate of co-disposal.

7.7.3 Spent battery recycling initiatives will reduce the concentrations of mercury and cadmium going into co-disposal sites provided the collected batteries are disposed of by another method, or the metal content is recovered. The conversion to mercury-free alkaline cells and in time other mercury-free batteries will make the domestic mercury burden largely historical.

7.7.4 Engineered landfills represent a long term burden with respect to leachate or gas control and therefore represent a release threat associated with insufficient attention after landfill operations have ceased.

We feel that on the precautionary principle, wastes containing soluble and potentially soluble mercury and cadmium should be excluded from co-disposal landfills unless conclusive evidence can be shown that no environmental releases will occur.

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8. MERCURY AND CADMIUM IN SEDIMENTS

In this section we investigate aspects of mercury and cadmium associated with aquatic sediments.

8.1 Behaviour of Cadmium in the Aquatic Environment

8.1.1 The majority of cadmium entering freshwater is readily absorbed by particulate matter (suspended solids or deposited sediments) or dissolved organic matter and only a small proportion of the fraction of cadmium remaining in water can be expected to remain biologically available (Coughrey et al. 1983). Within rivers, the absorbed cadmium will be transported with the suspended solids or will remain within the bottom sediments. These bottom sediments are able to be resuspended at a later date allowing transportation of cadmium associated with the particulate matter (WHO 1992).

8.1.2 A small proportion of the cadmium entering the seawater system can be expected to become associated with suspended sediments (apart from manganese oxides) or dissolved organic matter (Coughrey et al. 1983). Hence the remaining high proportion (greater than 90%) can be expected to remain soluble and therefore biologically available.

8.1.3 Cadmium is present in sediments in various forms (Nriagu 1980). The readily bioavailable fraction includes cadmium adsorbed on cation exchange complexes. The potentially available fractions include inorganic solid phases, $CdCO_3$, $Cd(OH)_2$, CdS, chelated and insoluble organic-bound cadmium, cadmium precipitated or co-precipitated with hydrous oxides of manganese and possibly iron, and several other inorganic constituents of minor importance. The unavailable fraction consists of cadmium bound within the crystalline lattice of clay minerals. Changes in the chemical parameters controlling these forms will result in changes in the bioavailability of cadmium.

8.1.4 Redox potential, pH and salinity are probably the most important chemical parameters controlling cadmium speciation, and therefore bioavailability, in sediment-water systems. These parameters vary within the aquatic environment. Surface waters are generally oxidised whereas sediments are moderately to strongly reduced. The pH of seawater generally ranges from 7.8 to 8.3 and is relatively uniform whereas that of freshwater may fluctuate from 5.0 to 8.5. The pH of surface sediments may range from 6.1 to 9.0 whilst a slightly lower pH may be encountered in deeper sediments.

8.1.5 A study on the effects of oxidising and reducing conditions on the release of cadmium from dredged sediment suspensions found that significantly higher concentrations of cadmium were released from the sediments under oxidising as compared to reducing conditions (Nriagu 1980). Significant, long term releases of cadmium from sediments to overlying water occurs only under oxidising conditions (Nriagu 1980).

8.1.6 Under oxygen rich conditions, cadmium release from sediments is proportional to salinity, perhaps due to the formation of soluble inorganic complexes in the presence of increased concentrations of chlorides, carbonates and sulphates. Greater competition from high concentrations of calcium, manganese and sodium for exchange sites may also be responsible for increased release of cadmium. Over 90% of the cadmium bound to Rhine River sediments is mobilised upon entering the North Sea (Nriagu 1980).

8.1.7 Deposits of cadmium are present in sediments in rivers, estuaries and harbours throughout the UK. Disturbance of these sediments either by natural or anthropogenic processes can lead to releases of cadmium to the marine environment. Natural processes can cause the transport of river and estuarine sediments to the marine environment which will result in the release of cadmium due to the effect of increased salinity. Anthropogenic processes, such as dredging, can cause the exposure of moderately to strongly reduced sediments to oxidising waters which will also result in the release of cadmium.

8.2 Behaviour of Mercury in the Aquatic Environment

8.2.1 The behaviour of mercury in the environment is extremely complex and incompletely understood. Inorganic forms of mercury are transformed mainly by oxidation-reduction reactions (WHO 1976). Metallic mercury entering the aquatic environment will be oxidised to ionic divalent mercury in the presence of oxygen. This reaction is particularly favoured when organic substances are present. The ionic divalent mercury can form a wide variety of complexes with these substances. Ionic divalent mercury can also be formed by the breakdown of a variety of organic compounds in the aquatic environment. Once formed, ionic divalent mercury is absorbed by particulate matter.

8.2.2 In anaerobic conditions where hydrogen sulphide gas is present, the reaction of ionic mercury with sulphide ions to form highly insoluble mercury sulphide is important. Under these conditions mercury sulphide is very stable and will not normally undergo further transformations. However in the presence of oxygen, it can be oxidised to soluble mercury sulphite and sulphate thus allowing the metal to be involved in subsequent reactions. Under highly reducing conditions the formation of more soluble polysulphides occurs (ICES 1989).

8.2.3 Under appropriate reducing conditions ionic divalent mercury can be reduced to metallic mercury vapour. Certain bacteria are able to convert divalent mercury into metallic mercury (WHO 1976).

8.2.4 Microbial activity in aquatic sediments can result in the methylation of divalent mercury. Methylation appears to occur in both oxic and anoxic conditions, although the rate of methylation is greater under oxic conditions (WHO 1989). Once the methyl mercury has been released from the microbial system it is highly biologically available and will rapidly accumulate in aquatic foodchains (USEPA 1984). Under anoxic conditions it seems unlikely that significant quantities of methyl mercury are formed in the aquatic environment. Methyl mercury is very stable in seawater (ICES 1989).

8.2.5 If the conditions of pH are appropriate, volatile dimethylmercury can be formed from methylmercury. The dimethylmercury will diffuse from the aquatic environment into the atmosphere, where it is subject to rainfall. If the rainfall is acidic dimethylmercury is converted to methylmercury and this returns to the aquatic environment.

8.2.6 Mercury has a great affinity for suspended particulate matter, especially for organic particles (ICES 1989) and therefore deposits of mercury are present in sediments in rivers, estuaries and harbours throughout the UK. The disturbance of anoxic sediments at these locations by natural or anthropogenic processes can lead to the formation of ionic divalent mercury under oxic conditions and thence to methylmercury which is highly biologically available.

8.3 Implications

8.3.1 As discharges of cadmium and mercury from industrial facilities decrease, the quantities in sediments and the potential releases to the marine environment via the disturbance of these sediments become more important. We are aware that work is being undertaken in Hong Kong and California investigating techniques to immobilise metals in sediments.

The behaviour of cadmium and mercury in the aquatic environment and the presence of these metals in sediments in the UK imply that significant releases to the marine environment are possible. Dredged material contributes between 40 and 55 % of the loads to sea (DoE 1992). Further investigations are therefore justified as there may be potential for significant reductions in this area.

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9. MERCURY & CADMIUM IN THE CEMENT INDUSTRY

Introduction

In this section we examine mercury and cadmium emissions from the UK cement industry.

9.1 General

9.1.1 Between 1990 and 1994 cement production in the UK declined from 14.7 million tonnes to 12.5 million tonnes of finished cement. Some old technology wet process capacity has been demolished, removed and partially replaced with modern dry process capacity.

9.1.2 Essentially the cement producing process consists of heating a blend of raw materials (raw meal) to around 1,450 °C to produce cement clinker as shown by figure 9.1. The raw meal consists of limestone or chalk blended with clay or shale, giving a typical chemical composition of 79% $CaCO_3$, 13% SiO_2, 3.5% Al_2O_3 and 2% Fe_2O_3. Heating is primarily provided by combustion of a conventional fuel, which may be one or more of the following; coal, petroleum coke, heavy fuel oil or natural gas. Combustion takes place in a kiln into which the raw meal is fed and clinker and dust/flyash is extracted. The resulting gases are discharged via a stack after gas cleaning, typically in an electrostatic precipitator or fabric filter. The output clinker is ground to a powder, with the addition of about 10% gypsum.

9.1.3 There have been significant moves in recent years to displace a proportion of these "conventional" fuels with waste derived fuels, principally those derived from solvents and other industrial wastes (Recycled Liquid Fuels - RLFs) and scrap tyres. A recent report (ETSU 1996) estimated the 1995 UK consumption of such fuels in cement plants at 84,800 tonnes coal equivalent, representing a reduction of about 4% in coal consumed (assuming coal to be the fuel displaced). The same report estimates that it may be feasible to replace up to 50% of conventional fuels consumed by the cement industry by waste derived fuels. The estimate for 1995 indicated the following split of waste derived fuel types consumed (on a tonnes coal equivalent basis):

- RLF 65%
- Scrap tyres 30%
- Others 5%

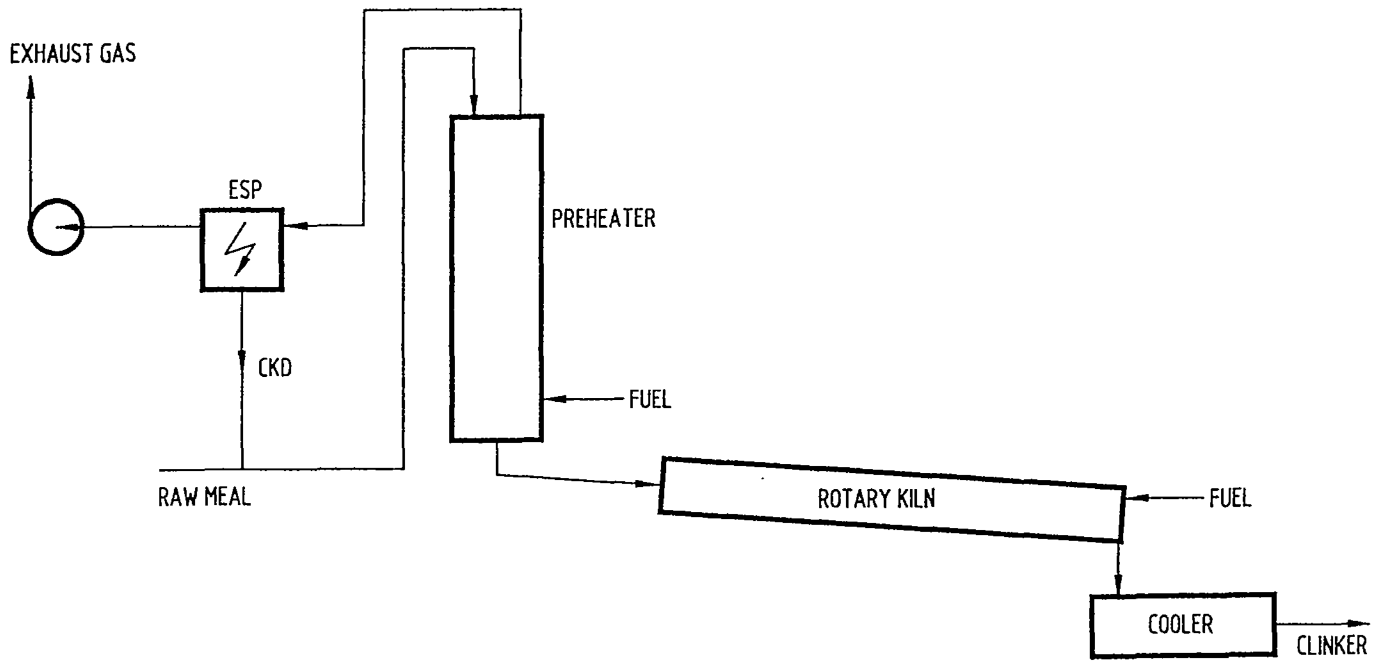

Figure 9.1 Simplified Process Flow Diagram - Cement Clinker Production

9.1.4 Mercury and cadmium are present as a trace contaminants in the raw meal and the fuel input. Estimates from cement industry sources give the cadmium and mercury content of these in the UK as:

Table 9.1 - Cement Industry trace contaminants

Material	Cadmium Content mg/kg	Mercury Content mg/kg
Raw meal - blend of limestone/chalk/shale	0.1 - 0.8	0.02 - 0.3
Coal*	0.4	0.1
Petroleum coke	0.1	<1.0
Recycled liquid fuel (maximum specified content: actual content typically lower)	40	20
Scrap tyre fuel	4.0 - 12.0	1.0

* ETSU 1993 data

9.1.5 Production of one tonne of cement clinker typically requires the consumption of the following quantities of raw materials and fuel;

Table 9.2 - Cement clinker production

Material	Quantity consumed per tonne of cement produced (tonne)
Limestone	1.24 - 1.28
Clay	0.31 - 0.32
Coal	0.18
TOTAL	1.73 - 1.78

9.1.6 The 0.73 - 0.78 tonne excess in the total mainly appears as CO_2 in the exhaust gas. Any mercury and cadmium input to the process is released either in the clinker, in the emitted flue gas (including any particulate matter) or in the Cement Kiln Dust (CKD) arrested by the gas cleaning equipment. Some of the lattermost may be included in the cement product.

9.1.7 The IPC Guidance Note for the cement industry, S2 3.01 (Environment Agency 1996) supersedes the Chief Inspector's Guidance Note IPR 3/1 (HMIP 1992) and provides details of release levels for kiln exhaust gases and all other contained releases under the following burning conditions;

- combustion burning no hazardous waste materials;
- combustion burning 40% or more hazardous waste;
- combustion burning 40% or less hazardous waste.

For the first two cases, no release level guidance for mercury or cadmium to atmosphere or water is given. For the third case, mandatory limits on emissions to air are given, which include cadmium (in combination with thallium) and mercury.

9.2 Mercury

9.2.1 Mercury enters the cement process in the fuel and raw materials. Mercury in the cement kiln is volatilised and joins the exhaust gas stream. The common view *is that* the mercury would then be largely emitted as vapour phase in the stack gases, with very small amounts condensing onto the CKD (up to 25 mg/kg) removed by the electrostatic precipitators. Most of this dust is recycled either to the kiln, or to the cement mill feedstock, thus effectively immobilising trace metals present in concrete. A small proportion may be disposed to landfill.

However, there is evidence to show that this may not be the case.

9.2.2 Verification of the mercury mass emitted to atmosphere by measurement is notoriously difficult at the low concentrations involved. The findings of recent tests at a UK works, according to industry sources, suggest that over 90% of mercury is captured in the clinker, with less than 10% released elsewhere, including via the stack.

9.2.3 The variability of data from a number of plants in the USA is attributed (Sarofilm et al 1994) to difficulty of measurement at concentrations close to the detection limit. Tests on German plants described (Wiesweiler et al. 1992) use a mass balance technique to estimate the proportion of vapour phase mercury emitted in the stack gases, having measured the quantity of mercury contained in the fuel, raw materials, arrested/emitted flyash and clinker. The results indicate that over 90% of the mercury input to the process is emitted in the vapour phase via the stack.

9.2.4 These apparently conflicting findings are indicative of the uncertainty which surrounds the mass of mercury emitted to the atmosphere in the cement production process.

9.2.5 Mercury release from kilns burning waste fuels containing mercury can be 2 to 3 times higher than those burning conventional fuel. The relatively high maximum mercury concentration permitted in one RLF specification would, if contained in the fuel as-burnt, lead one to expect higher emissions. However, cement industry sources indicate that recent tests on plants burning 50% RLF/50% coal have shown that mercury emissions to the air do not significantly change as compared to those associated with operation burning 100% coal. This is probably because the actual mercury concentration in the RLF is significantly lower than the maximum specified, combined with the fact that the dominant input of mercury to the process is in the raw meal, not the fuel. Industry sources do not believe that mercury content is considered when selecting raw materials.

9.2.6 Tests carried out on a limited number of cement works in the USA and Europe indicate that the annual mercury release from UK cement kilns to atmosphere lies between 600 and 3,000 kilograms. This equates to a release factor of 57 to 285 milligrams mercury per tonne cement produced.

9.2.7 In 1982, the estimated total mercury release to air was 2,500 kilograms (Hutton et al. 1986). As cement production for 1982 was 13.457 million tonnes, this equates to a release factor of 186 milligrams mercury per tonne cement produced. The mercury content of solid wastes is expected to be negligible.

9.2.8 Using a mass balance approach to estimate the total UK mercury release to air for 1994, the figure lies between 338 kilograms (assuming 10% released via stack) and 3,038 kilograms (90% released via stack). This equates to a release factor of 27 to 243 milligrams mercury per tonne cement produced.

9.2.9 Adsorption filters using activated coke media have proved to be particularly effective for mercury removal. At one European cement plant burning waste fuels, activated coke is installed as a fixed bed filter on the dust free exhaust stream after the electrostatic precipitators. The coke is replaced after the heavy metal concentration reaches a predetermined limit. No information is available on disposal of the contaminated activated coke material.

9.3 Cadmium

9.3.1 Cadmium derived from the raw materials or the fuel is volatilised in the kiln and travels with the exhaust gases to the pre-heater at the feed end of the kiln. Here the less volatile heavy metals are expected to condense in the relatively cold raw meal and therefore return to the sinter zone of the kiln. Thus an internal recycle is created. Cadmium remaining in the exhaust gas from the pre-heater condenses onto the dust particles present which are arrested by the electrostatic precipitators as CKD. CKD can contain up to 60 mg cadmium per kg dust. This creates an external cycle, though CKD addition to the cement mill feedstock is now permitted under BS12:1991.

9.3.2 Cement industry sources indicate that recent tests on plants burning 50% RLF/50% coal have shown that cadmium emissions to the air do not significantly change as compared to those associated with operation burning 100% coal. This is because, despite the potentially higher cadmium content of the RLF compared to coal (as permitted in the RLF specification), the dominant input of cadmium to the process is in the raw meal, not the fuel.

9.3.3 Measurements made reveal cadmium capture rates of up to 99.9% of the mass introduced to the process. 20 - 40% is present in cement clinker, 50 - 60% in CKD and a maximum of 2% is released in the exhaust gas. Recent emission estimates show an annual cadmium release to atmosphere of between 90 and 190 kilograms. This equates to a release factor of 0.009 to 0.018 milligrams cadmium per tonne cement produced.

9.3.4 In 1982 the estimated cadmium release was 1,000 kilograms/year (Hutton et al. 1986). Cement production for 1982 was 13.457 million tonnes equating to a release factor of 74 milligrams cadmium per tonne cement produced. Improvements in gas treatment may account for the improved efficiency since 1982.

9.3.5 Solid wastes from cement production are landfilled in municipal sites or in privately owned quarries. In 1982, approximately 21 tonnes of cadmium per year were landfilled (Hutton et al. 1986), equivalent to 1.5 grams per tonne cement. Addition of CKD to the cement mill feedstock, now permitted under BS12:1991, will tend to reduce the proportion of cadmium landfilled and increase that appearing in the cement. That appearing in the cement will become a constituent of concrete and be immobilised chemically therein.

9.3.6 Minor fugitive dust emissions from ancillary processes such as raw materials and coal grinding will contain trace quantities of mercury and cadmium at the concentrations of the feed materials.

9.3.7 Aqueous streams may be present if wet meal preparation is carried out. These waste waters will contain mercury and cadmium as trace contaminants at the concentration of the raw meal materials.

9.4 Conclusions

9.4.1 Cement production has been shown to be a potential sink to immobilise cadmium (and other non-volatile heavy metals) in a concrete matrix *suitably resistant* to long term leaching. However, wastes containing excessive chloride concentrations, such as residues from wet, dry or semi-dry gas scrubbing systems cannot be added into cement materials as BS 12:1991 limits the chloride content of cement to < 0.01% m/m. Cadmium emissions have been shown to increase approximately linearly with increasing cadmium input.

9.4.2 Measuring volatile metal vapours in exhaust stack gases is complicated by the low concentrations of the trace elements with values close to or below their detection limits, and also by the inability to capture volatile vapours in stack sampling systems, a problem of major significance with mercury. In Germany and the USA, a mass balance approach has been used to establish mercury release.

9.4.3 In a conventional pre-heater pre-calciner cement kiln layout with a main kiln exhaust stack, an alkali by-pass stack (if required for raw materials process reasons) and a clinker cooler stack, there is a substantial difference in the gas distribution of metals between the three stacks. Mercury in its vapour phase is preferentially emitted from the kiln exhaust stack, elements such as lead, cadmium, potassium and sodium, which re-cycle internally due to their volatility, concentrate in the by-pass stack, and refractory materials such as barium, chromium and nickel concentrate in the cooler stack. More recent kiln layout development based upon further energy efficiencies has dispensed with the clinker cooler exhaust stack and all waste heat from the cooler is now transferred to the pre-heater and pre-calciner. Thus the refractory metals could be expected to be emitted via the by-pass stack in this new configuration, but we cannot substantiate this.

9.4.4 Overall the cement industry does not represent a direct threat of mercury and cadmium release to water. However, spent gas cleaning materials containing mercury and some cadmium may represent a long-term aqueous release threat if landfilled under inappropriate conditions.

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10. MERCURY AND CADMIUM IN COMBUSTION PROCESSES

In this section we review mercury and cadmium releases to water originating from combustion processes. We have restricted our comments to combustion processes where trace metal contamination occurs, such as incineration and fuel combustion. This excludes the ferrous and non-ferrous smelting industries where volatile metal capture and recovery is well established.

There has been a large amount of investigative work on the complexities of combustion process residues and releases, both in the UK and abroad. It is beyond the remit of this study to report the current literature in detail. However, we present an overview concentrating on liquid discharges from the combustion process or from the residues produced.

The emphasis of this section is on waste combustion, as this activity is likely to increase in the next 5 years and this is where the maximum risk to water lies.

10.1 General Aspects of Combustion Processes

10.1.1 Large quantities of trace metal contaminated materials are burnt in the UK, usually at temperatures over 850°C. Historically coal combustion for heat, power and metal production represented the largest release of combustion products to the environment. This continues to be the case, though coal is being displaced by natural gas in electricity generation, a trend which is expected to continue into the early years of the next century.

10.1.2 In recent years, there has been increased activity in the incineration of waste materials, either simply as a concentration step prior to landfill, or additionally as a means of renewable energy generation (waste to energy plants). The Non Fossil Fuel Obligation (NFFO) (Van Santen 1993) initiative is an incentive to those wishing to generate electricity from waste materials and other non-fossil fuels.

10.1.3 The Environment Agency and Local Authorities regulate most incineration and combustion processes in the UK. Guidance to inspectors framing IPC Authorizations on release limits for mercury and cadmium is published for most Part A processes; typically between 0.1 and 0.2 mg/Normal m^3 (Van Santen 1993). Higher concentrations may be possible for Part B processes where total metal content, including mercury and cadmium, is 5.0 mg/Normal m^3.

10.1.4 In waste combustion the processor often has little or no control over the mercury and cadmium content of the material received, although sorting and segregation at source reduces the metals content of municipal solid waste. Mineral burning industries, including coal and oil combustion, may be able to source less contaminated materials or reduce the metal content by other means. Coal combustion and cement manufacture are discussed in sections 6 and 9.

10.1.5 If the trace metal content of the raw materials cannot be reduced by preliminary processing or sourcing of alternative materials, then gas cleaning to recapture volatilised metals is usually necessary to meet authorised stack gas emission limits.

10.1.6 Solid fuel combustion potentially produces four immediate waste streams to the environment, excluding other emissions concerned with raw materials storage and handling (ETSU 1990). These are:

Table 10.1 - Combustion Process Waste Streams

Waste Stream	Characteristics
Heavy (bottom) Ashes	Typically grate ash consisting of inert slag and cinders. Contains most of the non-volatile metals with varying fractions of the more volatile metals.
Fine Ashes	Typically fly ash consisting of fine dust particles, char, partial organic oxidation products, dioxin. Fly ash is typically enriched in cadmium and lead. May also contain residual solids from dry or semi-dry gas cleaning.
Stack Gases	Typically contains ultrafine particulate, NOx, CO, CO_2, some acidic gases and volatile metals particularly mercury. Concentrations depend on abatement technology, fuel composition and combustion conditions.
Liquid Effluent	Arising from a number of sources such as wet scrubbing systems, ash quenching, sludge thickening and dewatering, slurry transport and runoff from disposal sites.

10.1.7 Mercury and cadmium derived from the material burnt, or from gas cleaning reagents, will be present in varying quantities in each release stream. The quantities present in the fine (fly) ashes and liquid scrubber effluent (if applicable) depend on the gas cleaning system characteristics.

10.1.8 The quantities of these residue streams vary from process to process, site to site, although at individual plants releases are thought to be consistent (Mitchell et al.). For grate based municipal solid waste incineration, typical residual quantities are (Petersen 1986);

- bottom ash - 220 to 300 kg/tonne dry waste;
- arrested fly ash (including residual solids from dry or semi-dry gas cleaning, if installed) - 10 to 40 kg/tonne dry waste;
- flue gas - 4,500 to 6,000 Normal m^3/tonne dry waste;
- wet scrubber liquors - 550 litres/tonne dry waste (Reimann 1986) (if wet scrubbing installed).

Some fine dust will escape with the flue gases. Fluidised bed combustion produces more fly ash and little or no bed ash. Boiler blowdown is unlikely to be contaminated with cadmium or mercury.

10.1.9 The large masses of fuel materials burnt mean that even trace contaminants represent a significant release to the environment in mass terms. Estimates of the total amounts of material burnt together with the concentrations of trace materials present are subject to considerable variation. Table 10.2 summarises typical data.

10.1.10 Irrespective of the combustion fuel type, the majority of the cadmium, and virtually all the mercury, are volatilised into the gas stream. In flue gases, the vapour phase cadmium associates with and enriches the sub-micron particulate matter fraction, whereas mercury tends to remain in the vapour phase at flue gas temperatures over 130°C (Brunner et al. 1986) as simply represented below:

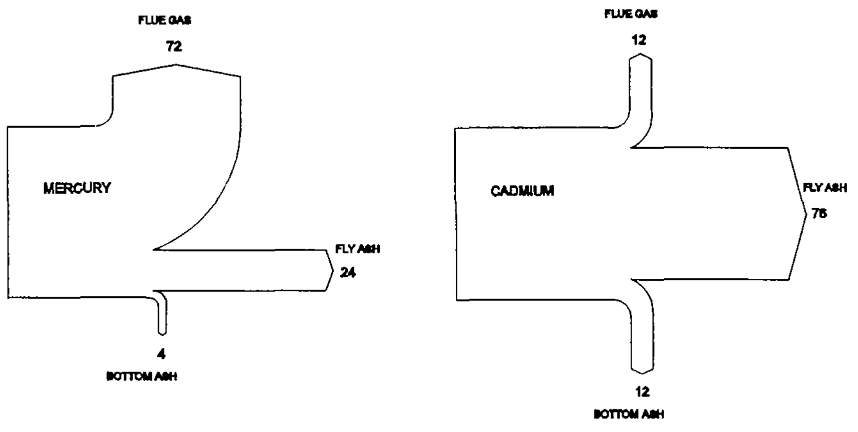

Figure 10.1 Partitioning of Mercury and Cadmium

10.1.11 The extent of partitioning will depend on other process combustion characteristics (ETSU 1990) such as temperature, turbulence and time, together with combustion control. The presence of abatement technology will remove toxic metals to an extent depending on the technology type. Wet scrubbers will remove some mercury, but the system which has been selected on most new and retrofitted municipal solid waste incinerators in the UK is injection of activated carbon prior to the particulate removal stage. The resulting residue, which contains mercury captured by the activated carbon, is arrested (normally by fabric filters) with the fly ash and other gas cleaning residues and is disposed intimately mixed with them.

Table 10.2 - Typical Characteristics of Solid Materials Burnt and Ashes Produced

Combustion Fuel	Annual Tonnage Burnt	Ash	Fuel Metals Content (dry weight)		Fly Ash Metal Content		Bottom Ash Metal Content	
	tonnes x 10^3	% weight	Cadmium mg/kg	Mercury mg/kg	Cadmium mg/kg	Mercury mg/kg	Cadmium mg/kg	Mercury mg/kg
Coal Combustion	77,000(2)	10.2	0.4	0.1	40	1*	4	1
Municipal Solid Waste(3)	1,750 estimated(4) (approx. 5% of arisings)	31.5	10 - 40	0.1 - 7	40(a) 100(b)	7(a) 80(b)	55	1
Clinical Waste(5)	250(6)	11.4	-	-	86	12	17	2
Paper Recycling Rejects(7)	?	4.2	1.4	<0.1	-	-	-	-
Poultry Litter	260(8)	9.0	6(9)	?				
Refuse Derived Fuel Pellets)	65(9)	15	9.8	0.3	690*	4*	2.5	1
Straw	160(9)	4.8	3	1	-	-	10	10
Waste tyres	80 estimated (confidential source)	11.6	8	1	20*	1*	25	1
Wood	?	0.85	<0.2	<0.04	6.5*	1*	1.5	1
Special Waste	200(4)	ND	?	?				
Sewage Sludge	72(4)	4 - 7	3.8(4)	2.9(4)	10.7	0.27	-	-

Sources - 1- ETSU 1993, 2 -DTI 1996, 3 -Carlson 1986, 4-DoE 1996, 5- ETSU 1993, 6-DTI 1995, 7-Mitchell 1992, 8-Modern Power Systems 1996, 9-HMIP 1995.

ND - Not Determinable
* - no fly ash collected, concentration in grit
a - historical: electrostatic precipitator only
b - modern: flue gas cleaning with lime and activated carbon injection plus fabric filter (figures from single plant performance tests)

10.1.12 The effect of this abatement technology will be to modify the diagrams in Figure 10.1, especially for mercury. A much higher proportion will appear in the fly ash and much less in the flue gas. However, we are not aware of any data from tests done to date on these incinerators which enables mass balances and partitioning diagrams to be produced. Tests which have been carried out have generally been to demonstrate compliance with IPC Authorizations and suppliers' guarantees, and do not include all measurements necessary for mercury and cadmium mass balances.

10.1.13 Although trace metals are initially present in dispersed low concentration, metal enrichment in specific waste streams occurs, particularly in fly ash. In addition to Table 10.2, some UK analyses for waste incineration residues are:

Table 10.3 - UK analyses for waste incineration residues

Incinerator	Cadmium mg/kg	Mercury mg/kg
Advanced Clinical Waste(1)		
- arrested fly ash	58	24
- grate ash	18.5	2.05
- emitted particulate	604	<385
Typical municipal solid waste(2)		
- arrested fly ash	275	4.1
- grate ash	58	<0.3
- emitted particulate	650	24
Fluidised Bed Sewage Sludge(3)		
- arrested fly ash	10.77	0.27
- emitted particulate	47	-
Multiple Hearth Sewage Sludge(4)		
- arrested fly ash	1,560	0.48
- grate ash	8.8	0.13

Source - Warren Springs Laboratory reports: 1-LR843, 2-LR875, 3-LR870, 4-LR908

10.1.14 Again, this data does not reflect recently-installed stack gas treatment plant, the effect of which is generally to increase the concentration of metals in arrested fly ash. The concentration in emitted particulate may also be increased, but the concentration of such particulate in the emitted stack gases will substantially reduce.

10.1.15 In addition to releases during and immediately after combustion, there is a long term leachate risk to ground and surface water derived from soluble metal forms from solid residue disposal.

10.2 Combustion Processes in the UK

10.2.1 Industrial scale combustion of different fuel materials is likely to change significantly from 1993 to 2010.

10.2.2 Coal combustion is decreasing and solid waste incineration is currently undergoing major changes. Most existing incinerators were due to close on 30 November 1996, as they were unable to meet new emission limits which became applicable thereafter. Some (generally those which generate revenue from heat and/or electricity sales as a result of the existence of heat recovery facilities) have been retrofitted with compliant emissions abatement plant. New compliant plants have recently been commissioned, are under construction or are in the planning stage.

10.2.3 It was anticipated by the 1993 Royal Commission that new incineration capacity will have regained 1993 levels by 2001, and that further increases will occur in the 21st century. It is clear that data on municipal solid waste incineration levels and the resulting emissions from recent years is not a reliable guide to those to be expected in the future.

10.2.4 Clinical waste used to be treated in small incinerators which were operated under Crown Immunity at hospitals. Since the introduction of the Environmental Protection Act in 1990, and the removal of Crown Immunity in 1991, these facilities have been required to upgrade to meet new emission standards, or close down. Most have elected to close and new plants have been constructed to replace this capacity. The new facilities use more advanced technology than the old, and early operational experience has been mixed. The long-term capacity (including any shortfall compared with arisings) resulting from the above is uncertain.

10.2.5 Combustion of other waste materials is increasing, but tends to be concentrated in a few locations. Two poultry litter incineration plants are in operation, and a third, larger plant is under construction. A single tyre incineration plant has been constructed and is in operation, but technical problems have limited its success. Sewage sludge incineration is expected to increase sharply (Royal Commission 1993) to the year 2000 as the Water PLCs intend to utilise this route for some of the sludge previously dumped at sea.

10.2.6 Incentives related to energy efficiency such as Combined Heat and Power (CHP) and NFFO are resulting in increased combustion of biomass derived wastes, such as agricultural waste and landfill gas. Other innovative processes such as liquefaction and gasification are developing (Van Santen 1993).

10.2.7 The 1993 Royal Commission reviewed the UK incineration situation. In 1991 there were over 200 waste incineration plants in the UK licensed by waste regulation authorities. These included 30 municipal solid waste incinerators with the remainder composed of clinical waste incinerators and privately owned general waste incinerators. In 1992, there were six sewage sludge incinerators operating, plus one plant in Scotland that also incinerated shredded municipal solid waste.

10.2.8 In addition to the licensed clinical waste incinerators, there may be up to 800 units operated mostly by NHS hospitals or trusts. Four plants incinerate special (hazardous) waste. Around forty incinerators are owned by chemical companies, six of these have an annual capacity in excess of 5,000 tonnes, and eighteen can burn between 1,000 and 5,000 tonnes per year.

10.2.9 Agricultural incinerators tend to be small scale units, although some 160,000 tonnes of straw are burnt annually to heat farm buildings.

10.2.10 The Royal Commission expected municipal solid waste incineration to decline to below two million tonnes per year (which our estimate for current incineration indicates to be accurate), and then to increase as new capacity is installed, such that some five million tonnes could be incinerated per year by 2001.

10.2.11 There is a balance to be considered between the relative costs and benefits of landfilling and incineration. This balance is strongly dependent on local factors which determine the cost and availability of landfill on one hand and the availability of waste and marketability of energy on the other. Planning issues have also had a strong influence on the successful promotion of incineration schemes.

The trend towards energy recovery and power generation from municipal solid waste combustion and financing under the NFFO initiative improves the economic position of waste to energy plants. The recently-imposed landfill tax has also boosted the viability of incineration.

10.2.12 Sewage sludge incineration is expected to increase rapidly, partly as the Water PLCs seek a disposal route for sludge currently dumped at sea, and partly because the quantity of sewage sludge for disposal is expected to increase due to additional treatment capacity required under the Urban Wastewater Treatment Directive. Estimates vary as to the expected increase in sewage sludge incineration. A figure of 500,000 dry tonnes per year seems to be a realistic figure (Royal Commission 1993) given the limited number of disposal options available, although it is possible that this may be an underestimate. However in 1994 the total incinerated was 72,000 dry tonnes.

10.2.13 Metal releases from crematoria are regulated by local authorities. Mercury and cadmium releases to air have been found to be less than 1 mg/Normal m^3 (Van Santen 1993), but highly erratic in this range (Warren Springs 1992). Ash disposal is not relevant and the opportunities for water contamination are minimal. If mercury collection devices, such as selenium filters, are fitted to crematoria stacks, then the spent selenium catalyst should be deposited in appropriate landfill where the mercury will remain immobilised.

10.3 Gas Scrubber Liquors

10.3.1 Wet gas scrubbing technology has not found favour to date in the UK for municipal solid waste incineration plants. On plants (abroad) where wet scrubbing is employed, on average 0.5 m^3/tonne dry waste wet gas scrubber liquor is produced (Reimann 1986) containing salts, metals and organic compounds removed from the gas stream. Such liquors are commonly acidic and contain high anion concentrations, especially chloride from acid gas scrubbing (10 to 20 g/l), together with dissolved metals (mercury typically 3 to 4 mg/l, maximum 15 mg/l) and organic materials.

10.3.2 Elemental mercury is difficult to remove from gases. High acid and chloride concentrations favour the formation of soluble mercury complexes. Under increasing pH values, divalent mercury Hg(II) can be reduced to mercury(I) and then disappropriate to Hg(o) and Hg(II); the elemental mercury is likely to follow the gas stream (Vogg et al. 1986).

10.3.3 These liquors are unsuitable for release unless treated. Treatment typically consists of neutralisation and hydroxide precipitation with a scavenger addition, such as TMT 15 or equivalent, to remove mercury chloride complexes. Such treatment is capable of achieving the concentrations suggested in IPCGN S2 5.01 of 20 µg/l for mercury and 40 µg/l for cadmium. The solid residues from this process may be dewatered further to a dry cake, or mixed with fly ash to form an insoluble material resistant to leaching.

10.3.4 TMT 15 and other scavenging agents have a high affinity for mercury and cadmium, forming virtually insoluble stable complexes (Degussa 1988), however, metal hydroxides formed by the main precipitation reaction are not stable and will leach cadmium and mercury at acidic pH values.

10.3.5 In most cases, scrubber liquors are discharged to sewer after treatment under sewerage undertaker control. In some cases, treated effluent is used for damping-down refuse and it is possible that a "zero aqueous emission" may become an EU requirement.

10.3.6 In a German plant, wet scrubbing liquors are treated by neutralisation, hydroxide separation and TMT 15 scavenger treatment. Cadmium and nickel are mostly removed by hydroxide precipitation, but residual mercury after hydroxide precipitation is around 2.5 mg/l so requiring the scavenger treatment. The fully treated effluent contained less than 0.05 mg/l mercury. The hydroxide/TMT sludge is mechanically dewatered and mixed with the electrostatic precipitator dust to give a compactable product that is difficult to leach and suitable for landfill; the so-called Bamberg model treatment (Reimann 1986).

10.4 Quench Tank Liquors

Quench tank liquors are discharged occasionally and tend to be of neutral to basic pH, containing readily soluble salts. These liquors may contain mercury and cadmium and should be tested before release. Quenched bottom ashes may leach liquors to the site drainage system, however mercury and cadmium content is expected to be low.

10.5 Ash Residues

Bottom Ash

10.5.1 Bottom ash constitutes between 75 and 90% of total ash and is composed mainly of mineral oxides (Williams 1990) together with non-combustibles. Soluble metals are removed if the ash is quenched. The heavy metal content is highly variable. In one simulated landfill study (Williams 1990) degradation of the ash occurred with significant leaching of metals. However, the 1993 Royal Commission found that grate ash had low levels of leachable pollutants.

Arrested Fly Ash

10.5.2 Although the proportion of waste-derived fly ash produced is 4% or less of the municipal solid waste dry weight, this still is a significant quantity in the UK. It is estimated that around 1.75 million tonnes of municipal solid waste will have been incinerated in 1996. If a moisture content of 31% is assumed, then up to 48,000 tonnes of fly ash were produced. If the fly ash cadmium concentration was 275 mg/kg (Warren Springs 1992), then this is equivalent to around 13 tonnes of cadmium deposited in landfills.

10.5.3 The release of mercury is difficult to assess, due to the scarcity of data on the concentration in fly ash of mercury captured by new gas cleaning systems and transferred to the fly ash stream. Results of tests from one UK incinerator fitted with activated carbon injection indicate a mercury concentration in fly ash of around 80 mg/kg. If this concentration is combined with the total national fly ash production from municipal solid waste combustion, would suggest an annual mercury deposition in landfills of eight tonnes.

10.5.4 There are some future considerations regarding cadmium content of arrested fly ashes including:

- the quantity of Ni/Cd batteries accumulating annually in the UK. This cadmium mass could enrich further fly ashes unless the battery collection schemes now being implemented are successful, or waste segregation/sorting is carried out. There are encouraging signs that NiCd collection schemes are achieving success;

- the quantity of cadmium in plastics is expected to reduce in accordance with the requirements of SI 1643 1993;

- the expected increase in municipal solid waste burnt, together with the higher particulate removal efficiency of gas cleaning systems, will produce more fly ash. Also the trapping of ultrafine fly ash, enriched with cadmium, will increase the mass of cadmium found in fly ash.

10.5.5 In one study sorting waste prior to combustion decreased mercury content from 0.96 mg/kg to less than 0.4 mg/kg and cadmium concentration from 13 to 9 mg/kg (ETSU 1990).

Metal Solubility

10.5.6 The metals present in the fly ash fraction vary in solubility according to pH and salt concentration. Fly ash dissolution in different elutriants, given as a percentage of the total metal present, varies as;

Table 10.4 - Fly ash dissolution in different elutriants, given as percentage of metal present

Metal	Residue	Distilled Water	1M HCl (0.1M HCl)	2M NaCl	H_2SO_4 (0.1M H_2SO_4)
Cadmium(1)	fly ash	55%	-	-	-
Cadmium(2)	fly ash	55%	98.8 (93.8)%	94%	97 (95)%
Cadmium(3)	fly ash	nd*	-	-	85***
Cadmium(3)	fly ash + lime reaction product	nd**	-	-	90***

Sources: 1- McKinley et al. 1992, 2-Gao et al. 1991, 3- Vogg et al. 1986

Key - * not detected; water pH 10
** not detected; water pH 12
*** H_2SO_4; pH 4

10.5.7 Metals, including cadmium, adsorbed onto fly ash particles may not be chemically bound (Gao et al. 1991). Thus mild solvents easily exchange cations, releasing the adsorbed metals in solution. The majority of metals leach from the ash residues within the first six months (Matsufiji et al 1985) of deposition.

10.5.8 Most work shows that under alkaline conditions the solubility of cadmium and other metals such as zinc and copper is minimal, although lead solubility can increase with pH (Vogg et al. 1986).

10.5.9 Leaching of cadmium will be related to the consumption of alkalinity. Flue dusts usually contain excess alkalinity, therefore large scale mobilisations can be expected only after a long period of time if acid rain is the acidity source. However, in co-disposal sites pH values of 5.0 are normally found so significant metal release is likely, although there is a high adsorptive material concentration present in freshly deposited landfills to restrict cadmium mobility. The presence of acid control reagents, such as lime, in the fly ash will assist in maintaining alkaline pH values and restrict cadmium release.

10.5.10 Heavy metals from waste incineration are much more likely to be soluble than those in coal fly ash (Mitchell 1992). This mobility will be greatly enhanced in co-disposal landfills operated as methanogenic bioreactors (Mitchell 1992). This concern was expressed by the 1993 Royal Commission who stated that solid residues from fly ash and scrubbers should not be landfilled with unprocessed municipal solid waste and that the then *HMIP* should ensure residues were sent for disposal in a form so as to minimise the risk of toxic substances contaminating groundwater. This recommendation was incorporated into the Special Waste Regulations 1996 (SI 1996 972), which came into force on 1 September 1996.

10.6 Present Disposal Activities

10.6.1 The quantity of fly ash produced is small compared to bottom ash. New incinerators and gas cleaning plants retrofitted to existing incinerators are designed for separate collection of fly ash, normally intimately mixed with solid residues from gas cleaning. SI 1996 972 classifies virtually all solid residues from municipal solid waste incinerators other than bottom ash as Hazardous Waste. The disposal route currently employed is to a controlled landfill, where mercury and cadmium should be immobilised.

10.6.2 Fly ash is now treated as a hazardous waste in the UK, and will not be co-disposed with municipal solid waste or bottom ash.

10.7 Options for Fly Ash Treatment

10.7.1 The various options for treating fly ash, none are economically self sustaining and some are experimental only, are;

- placing fly ash in sealed containers and landfill under inert conditions. This option was recommended by the 1993 Royal Commission, but could be expensive in material and handling costs;
- direct disposal into inert landfills. The cadmium and other toxic metals present would not leach under alkaline conditions, although lead will;
- vitrification is used in Japan where the cost of landfill is very high. We understand Germany and Switzerland are considering this option.

10.7.2 Ashes have pozzolanic properties that have enabled coal residues, such as PFA, to be sold as filler material for cement manufacture, road building, or as building materials. Fly ash residues from waste combustion are less suitable for this purpose due to their chloride and combustion residue content.

10.7.3 Alternatively fly ashes can be immobilised by 1:1 addition of portland cement. This produces a chemically stabilised reaction product and a low leachate cadmium content at pH 5.0. The disadvantage is the large increase in the mass of product (McKinley et al.1992).

10.7.4 Metal recovery is feasible using hydrometallurgical techniques. In some American states, fly ash is classed as hazardous waste requiring appropriate (expensive) disposal. Various hydrometallurgical techniques have been researched. One method (Gao 1991) (Mckinley 1992) uses HCl and NaCl elutriation of fly ash with followed by cementation using zinc dust to recover the leached metals. The leached fly ash residues were suitable for normal landfill and the zinc was recovered by electroplating. This process may become economically viable on the basis of the zinc recovery from the fly ash.

10.8 Conclusions

10.8.1 The published information shows clearly that mercury is quantitatively released to the flue gases during combustion. Vapour phase mercury chlorides dissolve into scrubbing liquors and elemental mercury adsorbs onto solid particles or remains in the gas stream according to the gas temperature. Modern flue gas cleaning systems use powdered activated carbon to adsorb mercury. The resulting residue is removed (usually by fabric filters) with the fly ash and other cleaning residues, for disposal to landfill.

10.8.2 Cadmium is mainly released to the flue gas stream although some will remain in bottom ash. In the flue gas, the cadmium quantitatively adsorbs to fine particulate matter which is arrested by the gas cleaning system or emitted with the cleaned flue gases.

10.8.3 Consequently, mercury is mainly associated with gas scrubbing residues and fly ash where activated carbon is injected prior to fly ash arrestment. Cadmium is associated with solid residues, particularly fly ash. Some cadmium will be present in wet scrubber liquors where applicable.

10.8.4 There are two waste streams from combustion processes that have implications for liquid effluent; wet scrubber liquors and arrested fly ash. High volume stack emissions, regulated by the Environment Agency in most cases, will also indirectly influence metal loads in rivers via land deposition and drainage.

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11. MERCURY AND CADMIUM IN THE OIL AND NATURAL GAS INDUSTRY

11.1 Oil

11.1.1 Information on mercury and especially cadmium in oil is limited. TNO (1994) suggest world-wide mercury concentrations range from 1 µg/kg to 30,000 µg/kg, the higher concentrations being generally found in North American oil fields where mercury ore is located in the same geology (Petroleum Industry Association personal communication). It is suspected that some previous estimates of the mercury content of crude oil in the UK and Europe are high due to the use of substantial amounts of North American data, and also use of older analytical techniques may have resulted in over estimates due to limits of detection being too high.

11.1.2 Reported world-wide cadmium concentrations in crude oil range from 0.3 µg/kg in Alaskan crude (Valkovic 1978) to 540 µg/kg (CEST 1991), however these data may not be reliable. The oil industry does not consider cadmium levels in crude to be significant, and what little information is available suggests that cadmium is found in lower concentrations than mercury.

11.1.3 TNO (1994) concluded that the average European crude has a mercury content of 30 µg/kg. TNO also estimate that Brent crude, which is typical of North Sea oil fields, and Arabian Heavy crude which is typical of Middle Eastern oil fields, have mercury concentrations of 1 to 3 µg/kg.

11.1.4 Although industry sources have stated that mercury in crude petroleum entering British refineries is not routinely measured, the UK Petroleum Industry Association (UKPIA) has quoted a single measured mercury concentration from a UK refinery as 5 µg/l (Department of the Environment 1996 Mercury in the Environment). This is equivalent to 6 µg/kg using Department of Trade and Industry (1996) conversion factor of 1 tonne crude oil to 1.19 cubic metres), and concurs with the lower estimates of mercury in oil, rather than higher ones used in previous studies.

11.1.5 The crude oil used in UK installations is assumed to be 65 per cent North Sea crude, 25 per cent Middle Eastern crude and 10 per cent of mixed origin. This mix, together with the conclusions of TNO for Brent and Arabian Heavy mercury contents, suggests that a figure of 3 µg/kg is a reasonable estimate for the mercury concentration of crude entering UK refineries, the value of 30 µg/kg (the European average) probably represents a worst case scenario.

11.1.6 The DTI (1996) reported total North Sea oil production in the UK sector for 1995 was 130 million tonnes of crude, and forecasted that this level of production will remain fairly constant up to 1999 and will then start to decline. This represents an annual release of 3.9 tonne mercury, using the European average concentration, or 0.4 tonne mercury using the upper value for Brent crude - which is a more likely estimate for North Sea crude. This does not however represent a total input of mercury to UK refining or related facilities, as much of the 130 million tonnes is exported.

11.1.7 The DTI (1996) data records show that during 1995 99 million tonnes of crude was delivered to: UK refineries (92 million tonnes); storage depots; and petrochemical plants. The annual amount of mercury entering UK refineries etc. is therefore approximately 3.0 tonnes using the European average, or 0.3 tonnes using the upper limits for mercury concentrations in Brent and Arabian Heavy crude.

11.1.8 The Government Statistical Service (1994) suggest that of the crude entering UK refineries in 1994 about 6 million tonnes was used as process fuel. Using the TNO figures and assuming that all mercury in combusted crude oil is emitted to the atmosphere, as suggested by Maxson et al. (1991), then an annual emission to the air of between 0.02 tonne and 0.18 tonne is likely, equivalent to an emission factor of 0.003 g/tonne to 0.03 g/tonne fuel for mercury, reported figures would suggest that an emission factor for cadmium would be significantly lower.

11.1.9 A proportion of crude oil is refined to fuel oil. The EMEP/CORINAIR Atmospheric Emission Inventory Guidebook (1996) suggests an emission factor for fuel oil of 1 g/Mg fuel for both mercury and cadmium, however, as this was derived from work done by Stobbelaar in 1992, and therefore pre-dates the work carried out by TNO suggesting a lower figure, this factor is probably an over estimate. It is unclear what proportion of crude is used as fuel oil, however it is likely that its contribution of mercury and cadmium to the environment during combustion is not significant

11.1.10 According to Pacyna and Nriagu (1988) the mercury content of other refined products (specifically vehicle fuel) is insignificant, therefore most of the mercury contained in crude must be removed somewhere during refining and processing. Valkovic (1978) suggested the most likely locations for removal are in heat exchangers and by deposition onto the surface of catalysts used in refining processes. As yet there is no quantitative information regarding the proportions of mercury removed from the oil at different stages during processing, or what methods of disposal are used for contaminated and damaged equipment. There is also no information relating to how much mercury, if any, is lost directly to environmental media during refining or processing.

11.2 Natural Gas

11.2.1 Natural gas contains trace amounts of mercury, but there seems to be no quantitative information regarding concentrations of cadmium, suggesting that cadmium has not been detected in natural gas in measurable quantities.

11.2.2 According the British Geological Survey (BGS) in 1992, the mercury concentrations in natural gas range from 1 $\mu g/m^3$ to 200 $\mu g/m^3$. The DoE report (1996) reported a concentration of 180 $\mu g/m^3$ in gas from the Groningen field

11.2.3 DTI data (1996) gave 1995 UK gas production as 75.3 billion cubic metres (with gas production forecasts suggesting that production will be from five to fifteen billion cubic metres higher in 1996, and will rise slightly over the next few years). Therefore assuming a worst case mercury concentration of 200 $\mu g/m^3$ for all producing fields, then total annual production of mercury in natural gas in the UK is 15 tonnes rising to approximately 20 tonnes by the year 2000.

11.2.4 According to the Government Statistical Service (1994), of the total production of 75 billion cubic metres, 69 billion cubic metres of gas are landed in the UK (the remainder being exported by the Netherlands from the Markham transboundary field). This represents a worst case mercury input of 14 tonnes mercury per annum.

11.2.5 Table 11.1 illustrates a selection of mercury concentrations in processed gas as received by British Gas. It shows that mercury concentrations in gas after processing, i.e. after water and heavy hydrocarbons have been removed, are substantially lower (up to 1000 times) than reported concentrations for unprocessed gas. This indicates that the majority of mercury is removed from the gas before use. Anecdotal evidence supports this assumption, as a number of fields have experienced mercury in elemental form forming amalgams in heat exchangers, pipe work and other equipment. Tannehill (1996) cited problems resulting from high mercury concentrations in Irish Sea gas fields (probably British Gas' Morecambe field) as reported at the 75th Gas Processors Association Annual Convention. There does not, however, appear to be any quantitative information regarding these occurrences. It is also unclear what method of disposal is employed for mercury deposited in this way.

Table 11.1 Mercury in Processed Natural Gas

Terminal	Field	Mercury Content (ng/m^3)*	Gross gas production 1995 (billion m^3)**
Bacton	Esmond (Hamilton)	70	0.036
	Leman (Shell)	31	2.017^a
	Sean (Shell)	27	0.929
	Indefatigable (Amoco)	26	1.303
	Leman (Amoco)	137	2.017^a
Barrow	Morecambe (British Gas)	110	10.074
Easington	West Sole (BP)	295	1.218
St Fergus	Various (Total)	7	4.661
Theddlethorpe	Various	15	8.352

Total production represented: 30.6 billion m^3 (40.6%)
Weighted average mercury concentration: 66.2 ng Normal m^3

* from Pacyna and Nriagu 1988
** DTI data 1996
a: Assumes an equal production split between Shell and Amoco in the Leman field.

11.2.6 A number of emissions estimates and factors have been calculated for natural gas combustion. Although this probably represents a small proportion of mercury entering the environment from the gas industry when compared with the potential large quantities released during extraction and processing. The factors assume that all mercury emissions from gas combustion are to the atmosphere.

11.2.7 For natural gas combustion CORINAIR (1996) suggest a mercury emission factor range of 0.05 g Hg/TJ to 0.15 g/Hg TJ. Assuming that one cubic metre of gas is equivalent to 37.98 MJ, the annual UK gas usage of 69.3 billion cubic metres is equivalent to 2,632,000 TJ, then the CORINAIR emission factor indicates an annual mercury emission from gas combustion of between 0.13 and 0.39 tonnes.

11.2.8 ERM (1996) used BGS figures for mercury in processed gas combined with Government gas consumption statistics, published in 1994, to generate an emission factor for gas combustion of 6.2 kg mercury per year. Using the ERM method of calculation, a revised emissions estimate can be calculated for 1995 as follows:

- Average mercury concentration of processed gas: 66.2 ng/m^3.
- Volume of natural gas: 69.3 billion m^3.
- Total mercury emitted through gas combustion in UK: 4.59 kg per year.

11.2.9 The implication of this estimate is that almost all mercury from natural gas is deposited in extraction of processing equipment, and is presumably disposed by some means. It also suggests that the CORINAIR proposed emission factor is an over-estimate.

11.2.10 Industry sources state that most mercury is found in the liquid gas phase, and hence is removed at the processing stage (as indicated by the BGS figures quoted in this report). Conoco have stated that this is the case at their processing facility (representing 20 per cent of UK gas production) and that the liquid phase is disposed of into the North Sea under IPC authorization. The authorization requiring them to be under 2 kilograms mercury or cadmium per year.

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12. IMMOBILISATION OF MERCURY AND CADMIUM

12.1 Introduction

12.1.1 Once toxic materials have been concentrated by clean-up technologies, they are ideally immobilised to prevent their subsequent release to the environment. In this section, we report the conclusions of several studies into the efficacy of various immobilisation techniques.

12.1.2 The basic immobilisation method is solidification in a stable, solid matrix which has a low permeability and a low rate of leaching. Potential immobilisation materials and techniques identified in the literature include:

- cement;
- clay processes (as used to cover flue gas desulphurisation wastes);
- bitumen;
- lime;
- thermoplastics and thermosetting resins;
- organic polymers and encapsulation;
- vitrification.

12.2 Cement and lime

12.2.1 Immobilisation is currently carried out in the UK by a number of hazardous waste contractors, whose preferred method involves mixing the waste with a cement grout, a fluid substance usually used for filling crevices. The advantages of cement grout over other immobilisation techniques include the following (Miller 1993):

- it is economical and readily available;
- it is established technology, requiring simple equipment;
- it is suitable for a wide range of materials in liquid, sludge and solid forms;
- it forms hydrates which are thermally stable with well documented physical and chemical properties;
- it is non-flammable;
- it has a high resistance to leaching over a range of pH conditions.

12.2.2 Leaching rates of hazardous materials from monoliths solidified by grout processing are measurable (Powell et al. 1992); cadmium compounds have a minimum solubility throughout the range of alkaline conditions.

12.2.3 A comparison of leaching from two solid sludge matrices, one formed from silicate and cement, the other fly ash and lime concluded that, "both methods appear to be technically feasible and economically attractive for immobilising certain toxic metals" (Johannesmeyer et al. 1985). The degree of immobilisation in the first mixture was directly proportional to the silicate content, but the silicate/cement technique was generally much more effective in immobilising cadmium. Both methods showed a loss of cadmium over a period of five weeks, and it is conceded that, "the structural integrity of the solid matrix over a long period of time is open to conjecture".

12.2.4 Leaching tests have been carried out on three cement types mixed with varying concentrations of cadmium. Only three of the leachate samples taken contained cadmium above the limits of detection (0.1 mg/kg), and it was concluded that, "cadmium is effectively retained in all cements and shows no sensitivity to leachate pH" (Heiman 1992).

12.2.5 Fly ash and Portland cement at a ratio of 1:1 apparently "primarily chemically immobilises" cadmium, and the mixture meets "environmental requirements". Although this is a simple approach, the volume of waste is effectively doubled. This is not a problem if a use can be found for the material (McKinley et al. 1992).

12.2.6 Concrete blocks made with fly ash and bottom ash have been washed with rain and the leachate found not to contain dissolved heavy metals at the detection level (Hasselriis 1988). Blocks tested in marine reefs were found not to have lost any heavy metals by leaching with sea water, and marine life thrived normally on them, though for an undisclosed period.

12.3 Bitumen

12.3.1 Fly ash, mixed with bottom ash, has been used for road construction for many years all over the world (Hasselriis 1988).

12.3.2 One recent study indicates that a road containing a fly ash sub-base built in the early seventies has not leached metals or any other hazardous materials into the surrounding soil or ground water (Collins 1992). Fly ash has also been mixed with bitumen in the ratio of 70:30 to produce a very strong, tensile material with 'negligible' toxic metal leaching characteristics, to be used in road or airport runway construction (Reimann 1986).

12.4 Organic Polymers and Encapsulation

12.4.1 There are measurable leach rates of hazardous materials from monoliths stabilised by urea-formaldehyde binding and polymer microencapsulation. (Powell et al. 1992)

12.4.2 Data on the leachability of mercury from immobilised ashes recovered from fossil fuel or solid waste combustion is sparse, because in most cases the mercury present in the initial fuel is lost to atmosphere as vapour. However, at least one study precipitated mercury in flue gas by reducing the temperature to around 150°C and employing a wet washing technique. The washing water was neutralised with calcium hydroxide, which also precipitates other heavy metals, and the mercury precipitated with trimercapto-s-triazine (TMT 15), produced by Degussa, Frankfurt. The degree of mercury precipitation is increased to 99% or more with this technique. The resulting Hg(II)-TMT 15 precipitate is allegedly very difficult to dissolve, resistant to acids and high temperature, and therefore has hardly any measurable leaching characteristics (Reimann 1986).

12.4.3 After being pressed into a compact, thick sludge of around 20% dry weight, the mercury-rich waste can then be mixed with dust from precipitators to produce a compactable and only slightly permeable product, a procedure termed "The Bamberg Model".

12.5 Thermoplastics and Thermosetting Resins

12.5.1 These are typically excluded on economic grounds.

12.6 Vitrification

12.6.1 Vitrification involves the use of electrical power to melt contaminated soil and solid material to form an inert glass product. A paper on the use of in-situ vitrification (ISV), where contaminated earth is vitrified by inserting a ring of electrodes into the ground and melting the material within, reported that any mercury present is vaporised and can be collected in an off-gas extraction system. It is uncertain whether cadmium would be similarly vaporised or actually immobilised. One advantage of vitrification is that organic compounds are 'destroyed' by the temperatures involved (Timmons et al. 1990).

12.7 Conclusion

12.7.1 The literature suggests that there are techniques available for reducing the leaching rate of mercury and cadmium. However, absolute immobilisation is theoretically impossible, and therefore it is the timescale of leaching which should be considered when selecting a technique for a given application. It will be many years before the results of on-going experiments yield reliable information on the long term "hold-up" of heavy metals. Therefore until a universally accepted 'best technique' evolves, selection will continue to be based primarily on economic grounds.

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13. FOREIGN LEGISLATION

13.1 Introduction

13.1.1 Overviews of foreign legislation relating to mercury and cadmium have been compiled by the OECD in their 1993 draft profiles on these metals. This data is reproduced below, with the information on cadmium reformatted to mirror that of mercury. However, the cadmium data was focused on identifying national risk reduction strategies and is therefore incomplete.

13.1.2 None of the following information should be regarded as definitive in 1996, but it is useful as an illustration of the western world's commitment to the reduction of mercury and cadmium in the environment. This report does not update the 1993 UK legislation presented in the following tables.

MERCURY

Table 13.1- Legislation for use of mercury in batteries

Country	Actions
Australia	Different regulations in different states.
Canada	Zinc-air batteries for hearing aids: a maximum of 40 mg/Ah rating on mercury content. Mercury reduction for cylindrical batteries: max. 0.025 % Hg by weight, decreasing to 0.02 % by July 1, 1993. Reduced mercury content in alkaline manganese button or coin batteries to max. of 25 mg per cell. Elimination of mercury in batteries by 1994-96 time-frame.
Denmark	EU directive (91/157/EEC) for batteries and accumulators containing certain dangerous substances. Directive implemented 1 January 1993.
EU	EU directive (91/157/EEC) for batteries and accumulators containing certain dangerous substances. Prohibition of sale of alkaline manganese batteries with more than 0.025 % Hg, except for those for prolonged use in demanding conditions where the limit is 0.05 % Hg. Directive implemented in member states from 1 January 1993. Alkaline manganese button cells and accumulators consisting of button cells exempted. The directive also gives an obligation to ensure that batteries are collected separately and raise the recycling-rate of batteries.
Finland	Regulations concerning the use, delivery, labelling, and collection of mercury-containing batteries are under preparation.
France	EU directive (91/157/EEC) for batteries and accumulators containing certain dangerous substances. Directive implemented 1 January 1993.
Germany	A ban of alkaline-manganese batteries with more than 0.025 % Hg from 1 January 1993. An obligation to label batteries containing more 0.025 % Hg or more than 25 mg Hg/battery cell. Strategy: To ensure that batteries are collected separately and raise the recycling rate of batteries.
Ireland	EU directive (91/157/EEC) for batteries and accumulators containing certain dangerous substances. Directive implemented 1 January 1993.
Japan	No information.
Norway	It is prohibited to manufacture, export, import or sell zinc/carbon and non-rechargeable alkaline manganese batteries which contain 0.001 % or more mercury by weight. After 1.1.95, the ban will include all types of batteries (even button cells). Packaging containing individual button cell batteries of the type mercury oxide, silver oxide, zinc/air or other types containing a total of 0.025 % Hg, shall be labelled with recycling symbol. Retailers who sell batteries that shall be marked/labelled, are obliged to accept comparable types of batteries for appropriate disposal from the consumers, free of charge.

Country	Actions
Sweden	An ordinance (1991) prohibits the use of some types of alkaline manganese batteries. Rules are included on labelling and collection of environmentally dangerous batteries.
Switzerland	1986 Regulations require gradual decrease of mercury in alkaline and manganese batteries. Under revision.
United Kingdom	EU directive (91/157/EEC) for batteries and accumulators containing certain dangerous substances. Directive implemented in phases beginning 1 January 1993.

Table 13.2 - Legislation for use of mercury-containing fluorescent tubes, electrical equipment, dental products, products for laboratory use, and thermometers

Country	Actions
Australia	Different regulations in different states; but no detailed information.
Canada	Future strategy: Instrumentation using mercury is being phased out and disposal of old instruments is done through toxic waste handlers. Dental amalgams be limited to high-traffic uses, such as molars for which there are no economic substitutes. Removal of amalgams before cremation may be an alternative in reducing emissions.
Denmark	General ban in preparation for sale of mercury and mercury containing products (more than 50 mg Hg/kg). Delayed ban and exemptions are given for different products. For instance, an immediate ban on mercury-containing thermometers, except for special purposes, as well as for dental fillings, will be implemented from 1 January 1995, with exemptions.
France	No information.
Germany	Mercury compounds or preparations containing mercury compounds must not be used or marketed for the following purposes; as antifouling dies, for the protection of wood, for the impregnation of heavy industrial textiles and for the production of yarns for heavy textiles, for water processing in industrial, business and municipal sectors independent of its use. Restrictions on use of mercury in thermometers, contacts and similar instruments are under preparation.
Finland	No specific regulation. Products containing substantial amounts of mercury are classified as hazardous waste when disposed.
Ireland	No information.
Japan	No information.
Norway	A ban on the production, import and sale of mercury-containing thermometers is expected to enter into force during 1993.
Sweden	No regulation of fluorescent tubes. From 1 January 1992, mercury in clinical glass thermometers are prohibited for import, manufacture and sale in Sweden. The same applies for other types of thermometers, measuring instruments and most electrical components containing mercury from 1 January 1993. Exemptions are given from the ban. It is not prohibited to use instruments that were bought before the ban came into force. The future strategy is to reduce all use of mercury. The Swedish Board of Health and Welfare has suggested a prohibition of the use of mercury in fillings of milk-teeth from 1 July 1993, and in fillings of young people up to the age of 19 from 1 July 1995. It is further suggested that the use of mercury amalgams in fillings of adults should cease after 1997.
Switzerland	Regulations in 1986 with a ban on use of mercury in all products. A list of exemptions are given with gradual reduction of mercury in the products according to technical possibilities.

Country	Actions
United Kingdom	There is no specific legislation controlling the supply of these products. Disposal of the products is covered by waste regulations.

Table 13.3 - Regulations for use of mercury in paints

Country	Actions
Australia	Restricted use.
Canada	A voluntary removal of mercurial compounds in interior latex paints has been done by major Canadian manufacturers, but mercury is still in use in exterior paints.
Denmark	Use forbidden since 1980.
EU	EU directive 91/188 bans the use of mercury in paint from 1992.
France	All mercury compounds banned from 31 March 1992. EU directive 91/188/EEC.
Germany	Forbidden since 1983.
Finland	No general ban or restrictions on use of mercury in paints. The use of mercury in antifouling paints was banned in 1992.
Ireland	All mercury compounds banned by end of 1992. EU directive.
Japan	Household paint must not contain organomercury compounds (regulated in 1973/74).
Norway	Mercury has not been used since 1970, owing to internal agreement among paint producers.
Sweden	No regulations exist. Swedish paint producers do not use mercury.
Switzerland	Use in paints forbidden for several years.
United Kingdom	Restriction in force for several years. EU directive with ban from 31 March 1992.

Table 13.4 - Regulations for use of mercury seed-dressing

Country	Actions
Australia	Restricted use in some states, e.g., as a fungicide in sugar cane sets. Forbidden in other states.
Canada	No registered pesticide with mercurial compounds is allowed.
Denmark	Forbidden since 1973, except for use in stock seed. From March 1992, all uses forbidden.
EU	EU directive 79/117, amended 1991 for phasing out in a few years.
Finland	Forbidden since October 1992.
France	EU directive 89/677 dated 21 December 1989. Ban in force from 21 June 1991.
Germany	Forbidden since 1982.
Ireland	Banned from 30 June 1991.
Japan	The last registered mercury-containing pesticide was in 1973.
Norway	Banned from 1 December 1991.
Sweden	Exemptions have been made after 1 July 1988.
Switzerland	Forbidden for use after 1991.
United Kingdom	Banned in 1992.

Table 13.5 - Legislation for control of mercury emissions to air, water and soil from energy production, refuse incineration, metal mining and production, gold mining, dental clinics, crematories, and other emission sources.

Country	Actions
Australia	Different regulations in different states, but no detailed information on limit values.
Canada	No detailed information except criteria for water: livestock water, 3 ug/l; drinking water, 1 ug/l.
Denmark	At present, no regulation of emissions to air from power plants. However, it is possible to adopt such regulation within the Danish Environmental Protection Act. Refuse incineration and power plants require an environmental approval from regional authorities. Danish regulations of emissions from waste incineration plants is based on EU directive 89/369. Emissions to water from industrial plants regulated by EU directive 84/156. Main Danish principle: reduce mercury emissions by best available technology. Crematoria must hold an environmental approval before January 1, 1994. Guidelines for design and operation of crematoria are issued but do not cover mercury. Some local authorities require permits for dental clinics limiting waste water to 5 g Hg/unit,yr.
EU	EU directive 89/369 sets limits on emissions to the atmosphere from new municipal waste incinerators and is as follows: 0.2 mg Cd + Hg/m^3. Emissions to water from industrial plants are regulated by EU directive 84/156 defining limit values and quality objectives for mercury discharges (to water) by sectors other than chlor-alkali industry.
France	EU directives. Special order prohibits the incineration of waste containing mercury.
Finland	Emissions to air, water and soil are regulated by the Air Pollution Control Act, Water Act, and Waste Management Act. Emissions limits are set on a case-by-case basis during the environmental permit procedures.
Germany	Energy production from burning of coal: Total concentrations of cadmium, mercury and thallium max. 0.2 mg/m^3. Wastewater: max. 0.05 mg Hg/l. Refuse incineration and crematories: Emissions to air max. 0.05 mg/m^3. Wastewater: max. 0.05 mg Hg/l. Metal mining and production: Wastewater from non-ferrous metal: max. 0.05 mg Hg/l. Facilities with high production capacity: max. load 1 g/ton produced metal (e.g. lead, copper, zinc). Dental clinics: Mercury load of raw wastewater from dental treatment must be reduced by 95% before mixing with domestic sewage, amalgam separators are used. Other legislation exists for mixed industrial wastewater (0.001 mg Hg/l).
Ireland	No information; but EU legislation in force.
Japan	Legislation for refuse incineration, metal mining and production, emissions to soil, emissions to water, fertiliser control act with limits for spreading of sewage sludge on agricultural soil.
Norway	Specific limits are set in the discharge permits for each industrial and waste incineration plant, according to the general legislation on environmental protection. Waste incineration: limit for emissions to air is 0.1 mg Hg/m^3. Metal mining and production: specific limits (0.1-8 kg/year). Regulations restricting discharges from dental clinics have been proposed. Installation of mercury separators and separate collection of mercury-containing waste will be required. Mercury-containing waste has to be treated as hazardous waste. Future strategy: Further reduction in emissions.

Country	Actions
Sweden	No specific limit applies for different activities. Instead, decisions on application permits are made on a case-by-case basis for each plant by the County Administrative Board and the National Licensing Board for Environmental Protection, which are empowered to prescribe measures to reduce pollution. Since 1985, dental clinics must install amalgam separators. For crematories, Sweden has ongoing projects aiming at installing selenium filters to minimize the mercury emissions. The long term goal is to phase out on a voluntary basis all uses of mercury in Sweden. By the year 2010, the goal is to have reduced the use of mercury by 75%.
Switzerland	Limits for emissions to air (1985). Limits for emissions to water (1975). Limits for emissions from dental clinics (1988). Limits for mercury in fertilisers (1986) and sewage sludge and compost (1992). Limits for mercury in soils (1986).
United Kingdom	Energy production from burning of coal: EU directives and use of the best available technology not entailing excessive costs (BATNEEC). Maximum emission limit to air 0.6 mg Hg/m^3, to water 0.02 mg Hg/l. Refuse incineration: EU directive 89/369. Metal mining and production and dental clinics: EU directive 84/156 with water quality objectives. No universal established limits. Crematoria: Similar to waste incineration plants; but no maximum limits for emissions to air. Emissions limits are set for individual sites through the authorization procedure.

Table 13.6 - Legislation for control of mercury emissions to air, water, and soil from chlor-alkali industry and future strategy for chlor-alkali industry

Country	Actions
Australia	No detailed information.
Canada	Criteria for air: Current mercury release under the Canadian Environmental Protection Act. 5 g/day/ton rated capacity in ventilation gases exhausted from plant cell rooms. 0.1 g/day/ton where the source is the hydrogen gas stream from denuders or the gases exhausted from end boxes or retorts. No release from the ambient air tank. Maximum total allowance in a plant is 1.68 kg/day. Liquid effluent under the Fisheries Act is 0.0025 Kg Hg/ton of chlorine produced. Elimination of mercury use by 2010.
Denmark	EU Directive 82/176. No production since 1991.
EU	EU Directive 82/176 defines the limit values and quality objectives for mercury discharges from chlor-alkali industry.
Finland	No information.
France	EU Directive 82/176. Elimination of mercury use by 2010.
Germany	EU Directive 82/176. Mercury emission factor is limited to 1.5 g/ton produced chlorine (Cl_2). Quality standards for waste water is 0.2 g/ton chlorine for a 24 hour sample. Elimination of mercury use by 2010.
Ireland	EU Directive 82/176.
Japan	No information.
Norway	The limit value for discharges to water is 0.25 g Hg/ton chlorine capacity and for emissions to air 2.5 g Hg/ton chlorine. The mercury-based process will be replaced with mercury-free process in 1998.
Sweden	Application permits are given case by case. Atmospheric emissions are today less than 2 g Hg/ton chlorine. Elimination of mercury use by 2010.
Switzerland	No information.
United Kingdom	EU Directive 82/176 with use of the quality objectives.

<u>Cadmium</u>

Table 13.7- Legislation for control of cadmium emissions from the cadmium plating, pigments and stabilizer industries

Country	Actions
Sweden	Use prohibited, listed exemptions for essential uses.
Denmark	Use prohibited, listed exemptions for essential uses.
EU	EU Directive (91/338/EEC). Lists of prohibited uses of cadmium compounds in specified plastics. Safety applications exempt.
	EU Directive (83/513/EEC). Limit value of 0.2 mg/l for cadmium discharges from following processes: zinc mining, lead and zinc refining, cadmium metal and non-ferrous metal industry, manufacture of cadmium compounds, pigments, stabilizers, batteries, phosphoric acid and phosphoric fertilisers and electroplating.
Netherlands	Import prohibition on pigments, stabilizers and plating material containing more than 50 mg/kg of cadmium. Several exemptions, mainly safety related.
Austria	Preparing prohibition. Proposals for ban on: pigments with a cadmium content >10 mg/kg, high zinc products with a cadmium content >100 mg/kg, zinc plated material with a cadmium content >20 mg/kg. Several exemptions, mainly safety related.
Germany	"Non-migration" principle applies to materials in contact with food, packaging, consumer items and toys. ie when used as intended, no colorant may transfer from the consumer item to food or saliva.
Switzerland	Use of cadmium in pigments is prohibited if state-of-the-art substitutes are available. The concentration of cadmium in plastics must be no higher than is necessary for the purpose intended. Plating/coating generally banned, exemptions listed.

Table 13.8- Legislation for uses of cadmium-containing soils, sludges and fertilisers

Country	Actions
EU	Directive (86/278/EEC) sets limit values for cadmium content in soil and sludge used in agriculture. Soil: 1-3 mg/kg dry weight (DW); Sludge 20-40 mg/kg (DW).
Denmark	Limit for cadmium in sludge for agricultural use: Presently : 1.2 mg/kg From 1995: 0.8 mg/kg Limit for cadmium in fertilisers: Presently 150 mg/kg, 110 mg/kg from July 1995, 50 from July 1998
Sweden	Limit for cadmium in sludge for agricultural use: Presently : 4.0 mg/kg From 1995: 2.0 mg/kg Limit for cadmium in fertilisers: 100 mg/kg.
Finland	Limit for cadmium in sludge for agricultural use: Presently : 3.0 mg/kg From 1995: 1.5 mg/kg Limit for cadmium in fertilisers: 50 mg/kg.
Canada	3 mg/kg (DW) agricultural soil 5 mg/kg (DW) residential soil 20 mg/kg (DW) for commercial / industrial use.
Japan	0.01 mg/kg soil 0.3 mg/l landfill sludge Limit for cadmium in fertilisers: 340 mg/kg.
Australia	Contaminated site soils: Investigation threshold: 5 mg/kg (DW) Action threshold: 20 mg/kg (DW) Limit (voluntary) for cadmium in fertilisers: from 1994, 500 mg/kg; from 1998, 400 mg/kg; from 2005, 300 mg/kg.
Switzerland	Limit for cadmium in fertilisers: 50 mg/kg.
Norway	Limit for cadmium in fertilisers: presently 100 mg/kg, in future 50 mg/kg.
Austria	Limit for cadmium in fertilisers: 275 mg/kg.
Germany	1 mg/kg guide value for farmland soils. Limit for cadmium in fertilisers: 200 mg/kg. (voluntary)

Table 13.9 - Legislation for uses of cadmium-containing batteries

Country	Actions
EU	Directive (91/157/EEC) concerns batteries containing more than 0.025% cadmium by weight. The directive contains demands on battery labelling, collection and consumer information, and the prohibition of such batteries in sealed appliances.
Austria	Regulations concerning labelling and collection of waste batteries.
Switzerland	Regulations concerning labelling. Batteries with >250mg/kg of cadmium can be prohibited if experience has shown that after use these batteries find their way into domestic refuse. Return and recovery requirement on user, manufacturer, dealer and supplier. Point of sale recovery advertising.
Sweden	Regulations concerning labelling and collection of waste batteries.
Norway	Regulations concerning labelling.
Denmark	Regulations concerning labelling. Fee imposed on NiCd batteries. Aiming for NiCd collection rate of at least 75%.
Japan	Regulations concerning collection of waste batteries.
USA	Regulations concerning collection of waste batteries. Several states demand manufacturers to develop recycling programmes.

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14. WASTE WATER TREATMENT PLANTS

14.1 Introduction

14.1.1 In this section we review the likely fate of mercury and cadmium at municipal waste water treatment plants. The majority of the mercury and cadmium discharged to the foul sewer, excluding that lost in storm overflows, is received at the treatment works inlet.

14.1.2 A waste water treatment plant acts as a metal accumulator between the discharge points, either industrial or domestic, and the sea. Metals are removed at every process stage, mostly captured into the sewage sludge stream. Some metal will pass through the treatment plant to reach controlled waters. The sludge solids, which contain much of the metal load received at the plant inlet, are stabilised and then dispersed or incinerated according to standing requirements.

14.1.3 Waste water received at a municipal waste water treatment plant contains a wide spectrum of metals derived from domestic, industrial and runoff sources. The Urban Wastewater Treatment Directive requires treatment of all sewage before discharge to controlled waters.

14.1.4 A recent report (Foundation for Water Research 1994) investigated diffuse sources of heavy metals to sewers in two sewerage catchments; Bracknell and Shrewsbury. Table 14.1 shows the sources of mercury and cadmium in the sewage.

Table 14.1 Sources of Mercury and Cadmium at 2 UK Sewage Treatment Plants

Source	**Cadmium**		**Mercury**
	Bracknell	**Shrewsbury**	**Bracknell**
Domestic	27.1%	30%	41.3%
Light Industry	33.6%	22%	9.5%
Commercial	10.7%	7%	49.0%
Runoff	27.9%	41%	-

14.1.5 At Bracknell, the domestic input for cadmium resolves further into 16% from washing machines, 11% from dishwashers, 3% from bathing and 70% from faeces.

14.1.6 The environmental fate of the metals present in the sewerage system is dependent on the type and extent of treatment at the waste water treatment plant. On this basis an overview of the mercury and cadmium removal and release mechanisms operating at a wastewater treatment plant is useful. It is stressed that metal removal and concentration performance is highly variable depending on physical, biological and chemical process factors which are generally site specific.

14.1.7 Sewage received at a treatment plant inlet will contain metals as various species. Their chemical state will influence the removal pathways together with the percentage removal and the ultimate disposal route.

Metals arrive at the works inlet as:

- insoluble, heavy particulate matter;
- insoluble fine suspended particles in solution;
- complexes with organic matter.

Peak metal loadings are likely to coincide with the working day and be diluted by 24 hour average sampling. Storm events will flush sewers of particulate matter including metalliferous solids.

14.1.8 The main metal bearing streams from treatment works and their environmental fate are:

- grit and detritus disposed as landfill or dumped on sewage treatment work sites;
- treated effluent discharged to controlled waters containing the residual toxic metals not removed by the treatment processes;
- sewage sludge solids after stabilisation treatment;
- sewage sludge combustion residues after incineration;
- gaseous emissions resulting from any of the above containing volatile species.

14.1.9 Accordingly the primary routes for metal removal from the liquid stream are;

a) grit sedimentation;

b) primary sedimentation (gravity settlement);

c) secondary biological treatment. Metals in solution are associated (concentrated) with the biomass which is subsequently diverted to the sludge treatment stream. There are several routes for removal of soluble and insoluble metal species including bio-accumulation;

d) tertiary solids removal treatments, such as sand filtration.

14.1.10 The percentage solubility of a metal is reported to increase throughout passage in a conventional treatment works (Stephenson et al. 1987); for example 60% of the cadmium may be present in soluble forms in treated effluent discharged to controlled water, whereas in settled sewage 78% of the cadmium was insoluble at one site.

14.1.11 Some sludge stabilisation treatment processes have the potential to release gaseous emissions of volatile metals to the environment. For example;

- anaerobic digestion takes place at 35°C under turbulent conditions. The digester gas produced is flared or burnt in boilers, engines or other combustion processes;
- sludge drying takes place at temperatures around 80°C which are sufficient to release labile volatile species from the sludge. Subsequent gas cleaning processes may not address toxic metals removal;

- sludge incineration will release all volatile or semi-volatile metals from sewage sludge into the fly ash, bottom ash or gas streams;

- composting processes and Thermophilic Aerobic Digestion; both require to attain 55 °C and could release volatile materials in the forced air stream.

14.1.12 Biological treatment processes including downflow percolating filters and activated sludge plant aeration tanks, especially diffused air processes, act to strip volatile materials from the wastewater flow into the gas phase.

14.2 Mercury at Wastewater Treatment Plants

14.2.1 Mercury present as large heavy particles, for example dental amalgam waste, will typically be removed as grit and detritus at the works inlet. No specimen analyses has been found for this stream.

14.2.2 Mercury balances to waste water treatment plants have been particularly difficult (FWR 1994). In the 1994 study at Bracknell, the calculated mercury load based on sampling data was some 40% of the actual load measured at the treatment plant. This shortfall was tentatively attributed to dentistry inputs.

14.2.3 Mercury present in sewage as fine particles or complexes with other ligands is removed in primary sedimentation. Mercury removal efficiencies of 57% and 54% at influent concentrations of 7 µg/l and 1.3 µg/l respectively are reported (Lester 1983) for primary sedimentation.

14.2.4 After primary sedimentation, residual mercury removal in activated sludge plants appears to be highly variable with removal efficiencies ranging from 17 to 97% (Stephenson 1987).

14.2.5 Combining the removal efficiencies of primary and biological processes, treatment plants can be expected to achieve at least 62% removal of the inlet mercury load (after grit removal). No information was found for single stage processes, such as oxidation ditches, and some coastal plants may be primary sedimentation only; therefore an overall removal efficiency of 60% is suggested as a working factor.

14.2.6 Mercury release to atmosphere from wastewater treatment and sludge stabilisation processes could be significant. In 1975 an American study of organo-mercury and elemental mercury emissions to air from central sewage treatment facilities was made in the USA (Soldano et al. 1975). A range of atmospheric mercury concentrations was measured and a correlation was established between population numbers served and downwind alkylated mercury concentrations. Atmospheric concentrations ranged from 0.12 to 15,875 ng/m^3 for elemental mercury and from 0.13 to 42,500 ng/m^3 for alkyl mercury.

14.2.7 A subsequent study (Warren Springs 1978) showed that the high atmospheric mercury concentrations measured at American waste water treatment plants were not detectable in the UK. Comprehensive measurements at three treatment plants showed weekly mercury concentrations did not exceed 0.02 µg/m^3 (mean 0.006 µg/m^3). These measurements included inorganic and organic mercury species.

14.2.8 Heated process technologies are the most likely sites of volatile metal species release. Mesophyllic anaerobic sludge digestion, as the most common sludge stabilisation technology, is the most likely source of volatile mercury release. Metals are likely to be associated with sulphide in the reducing environment of a digesting sludge, however the chemistry is complex and opportunities are likely to exist for formation of volatile methylated species and elemental mercury.

14.2.9 Currently some 50% of the UK sewage sludge production is anaerobically digested producing stabilised sludge for disposal plus digester gas with a high methane content. Large volumes of digester gas are burnt to recover the energy content, alternatively it is flared as a waste product.

14.2.10 A 1995 German study investigated volatile metals and metalloid species in sewage gases (Feldmann et al. 1995). Gas analyses from seven treatment works showed a large variation with a tendency for gases from thermophilic (>50°C) processes to contain metal or metalloid concentrations an order of magnitude higher than corresponding mesophyllic processes (35°C). Dimethyl mercury was detected in gas samples combined with unknown species including elemental mercury. The concentration range detected was 0.012 to 0.026 $\mu g/m^3$.

14.2.11 At an annual net sewage sludge production of around 1.4 million tonnes dry solids (ETSU 1993) at 80% volatile matter content, the net digester gas production is around 224 x 10^6 m^3 per year assuming 40% volatile matter reduction and gas production at 1,000 m^3 per tonne volatile matter destroyed. If mercury was present in digester gas at a concentration of 0.100 $\mu g/m^3$, this would be equivalent to some 220 grams mercury per year from this source, which is insignificant.

14.2.12 Gaseous emissions from sewage sludge incinerators contain mercury which is removed by gas cleaning systems. Emissions from sewage sludge incinerators are regulated under IPC.

Other Sources of Mercury

14.2.13 Historically a substantial quantity of elemental mercury was used as a seal/bearing in the central distributor column of rotating biological filters throughout the UK.

14.2.14 This mercury may be lost from the columns by mechanical failure, during maintenance, or during decommissioning operations. If spilt, such mercury may give a persistent load of inorganic and methylmercury in output streams.

14.2.15 A recent American study (Gilmour et al. 1995) found that of 157 grams of mercury released from a waste water treatment facility per day, 20 grams were derived from the influent sewage. The remainder of the mercury input was shown to be due to the percolating filters which were either equipped with, or had been equipped with, mercury seals on the distributors. Mercury lost from the seals over a period of time contaminated the filter bed resulting in elemental mercury release and methylmercury release. Most of the inorganic mercury lost from the filter beds accumulated in the humus sludge, the methylmercury concentration reduced primarily due to chemical or biological de-methylation.

14.2.16 Anecdotal evidence suggests that this situation may exist in the UK although the extent of such contamination is not known.

14.2.17 Not all rotating biological filters used mercury seals. We understand that the Water PLCs have replaced most of the mercury containing distributors with mechanical designs, although there are still likely to be a limited number remaining in use. Thus in some cases there may be a historical legacy associated with the use of this equipment.

14.3 Cadmium at Waste Water Treatment Plants

14.3.1 Cadmium in sewage is derived from industrial discharges, domestic sources and from road runoff. The majority of cadmium is derived from industrial sources. Cadmium has also been associated with the phosphate content of detergents although detergent industry sources refute this.

14.3.2 Cadmium removal efficiency in primary sedimentation processes varied between 25 and 60% with an average of 40% at influent concentrations between 5 and 24 µg/l (at 5 sites) (Stephenson et al. 1987); however removal efficiency averaged 72% at another site.

14.3.3 Following primary sedimentation, residual cadmium removal efficiency in activated sludge plants varied from 11 to 80% with an overall average of 46% (Stephenson et al. 1987). The insoluble cadmium fraction being removed most efficiently.

14.3.4 On this basis, overall cadmium removal efficiency for conventional activated sludge plants with primary sedimentation is estimated at around 68%.

14.3.5 Unidentified volatile cadmium species were detected in sewage gases at low concentrations between 0.004 and 0.007 $\mu g/m^3$ (Feldmann et al. 1995). On this basis gaseous cadmium emissions from treatment works are not expected to be significant.

14.4 Sewage Sludge Metal Concentrations

14.4.1 Most metals captured at a waste water treatment plant accumulate in the sludge stream. Consequently the metals content of the sludge is a good measure of the metal load received at the works which passes preliminary treatment.

14.4.2 Sewage sludge mercury and cadmium masses have been steadily decreasing since 1985 in response to the increased regulation. Sewage sludge metal data from landspreading activities (the most common disposal method) are not available, but metal loads in sewage sludge dumped at sea are available annually since 1985 (DoE 1996). Table 14.2 gives the mass of sewage sludge and the metal content. The sludge metal concentration is calculated from the dry solids and mass data.

14.4.3 Sewage sludge derived from large and often industrial conurbations is more likely to be dumped at sea (until 1998) and may present higher concentrations than from less industrialised catchments found in the south of England. Table 14.2 also includes an estimate of the mass of mercury and cadmium landspread using the DoE sewage sludge mass data combined with the metal concentration of the sludge dumped at sea.

Table 14.2 - Metal Content of Sewage Sludge dumped at Sea

Year		Cadmium		Mercury	
	Dry Solids dumped tonnes	Metal Content tonnes	Concentration mg/kg	Metal Content tonnes	Concentration mg/kg
1985	252000	3.77	14.96	1.35	5.36
1986	297000	3.84	12.93	1.37	4.61
1987	281000	3.73	13.27	1.35	4.80
1988	288000	2.92	10.14	1.17	4.06
1989	296000	2.68	9.05	1.14	3.85
1990	274000	2.06	7.52	1.07	3.91
1991	287000	2.15	7.49	1.06	3.69
1992	292000	1.95	6.68	0.97	3.32
1993	274000	1.31	4.78	0.75	2.74
1994	289000	1.10	3.81	0.83	2.87

Source - DoE 1996 Concentration data calculated

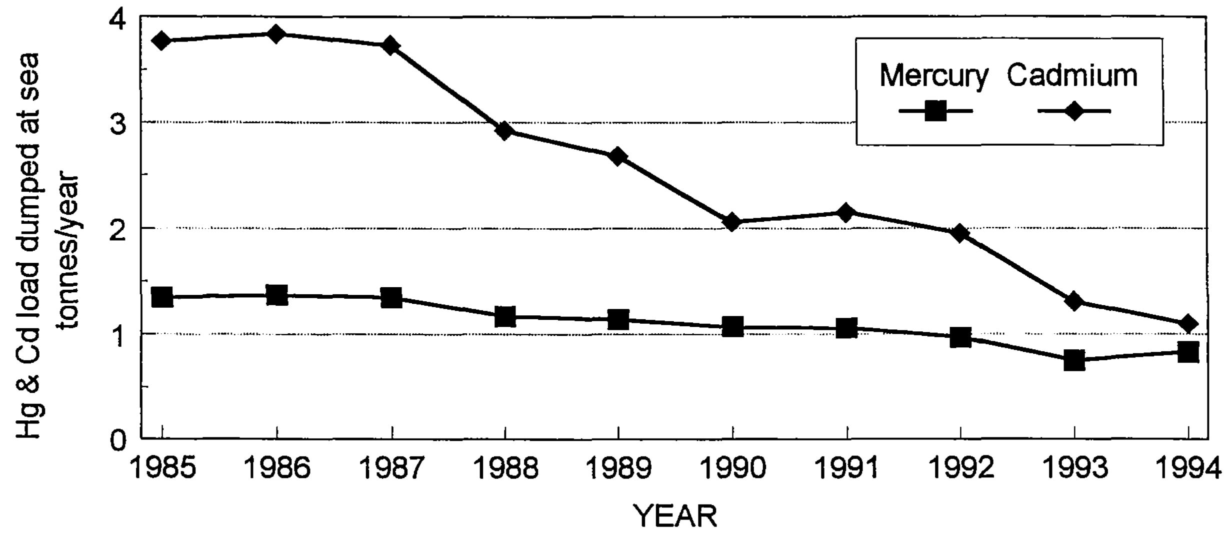

Figure 14.1 - Mercury and Cadmium Content of Sewage Sludge Dumped at Sea (from DoE data)

Table 14.3 - Metal Content of Sewage Sludge spread on Land*

Year		Cadmium		Mercury	
	Dry Solids spread tonnes	Metal Content tonnes	Concentration mg/kg	Metal Content tonnes	Concentration mg/kg
1989	535000	4.84	9.05	2.06	3.85
1990	551000	4.14	7.52	2.15	3.91
1991	503000	4.43	7.49	2.19	3.69
1992	483000	3.67	6.68	1.82	3.32
1993	506000	2.70	4.78	1.55	2.74
1994	504000	2.21	3.81	1.67	2.87

Adapted from DoE data 1996

* Includes other uses e.g. forestry, composting etc.

14.4.4 Table 14.3 assumes the mercury content of sewage sludge spread on land is the same as that dumped at sea; in reality it may be less as most sewage sludge dumped at sea is derived from large connurbations often with concentrations of industy. For the same concentration data, Table 14.3 and Figure 14.2 show the same trend for land spreading as for dumping at sea; cadmium mass continuing to reduce whereas mercury mass has stabilised.

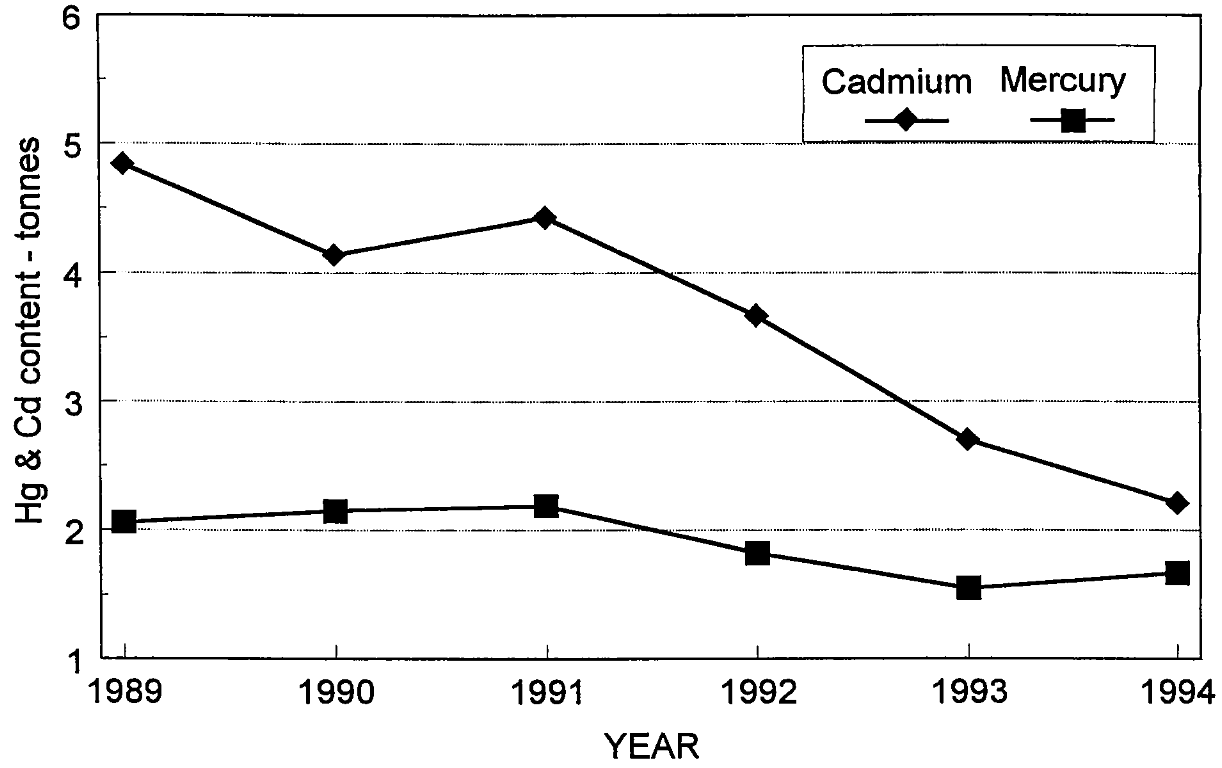

Figure 14.2 - Mercury and Cadmium Content of Sewage Sludge Spread on Land (from DoE data)

14.4.5 In 1994, 123,000 dry tonnes of sewage sludge were landfilled, 72,000 incinerated and 77,000 disposed by other means. This is equivalent to 1,039,000 dry tonnes sludge. At a cadmium concentration of 3.81 mg/kg and a mercury concentration of 2.87 mg/kg dry solids, then the total masses of cadmium and mercury in UK sewage sludge solids are 3.96 and 2.98 tonnes respectively.

14.5 Sewage Sludge Disposal to Farmland

14.5.1 Sewage sludge disposal to Agricultural Land is regulated by a Code of Practice (DoE 1989). The Code of Practice sets limits on the maximum quantity of sludge that can be applied to a unit area based on various criteria including the individual toxic metals content of the sludge. Cadmium concentration has historically been a limiting metal factor for sludge application to agricultural land and continues to be based on 1994 sludge metal concentrations. Sludge mercury may become limiting if cadmium contents reduce significantly.

14.5.2 Nearly 50% of the sewage sludge solids are disposed of to farmland under a tightly regulated programme. Annual returns detailed sewage sludge disposal are made to the Environment Agency.

14.6 Sewage Sludge Incineration

14.6.1 Sewage sludge incineration is expected to increase as Water PLCs seek new disposal routes for sludge previously dumped at sea. New incinerators are at the planning stages.

14.6.2 In 1991, some 69,000 dry tonnes of sludge were incinerated (equivalent to 6.5% of the total sludge production); by 1994 this had only increased marginally to 72,000 dry tonnes (DoE 1996). Sewage sludge incineration capacity is expected to increase to the end of the decade with up to 30% of the sludge production possibly being incinerated by the year 2000 (Royal Commission 1993). On the basis of a sewage sludge production of 1,400,000 tonnes dry solids per year, this will be equivalent to some 280,000 tonnes dry solids per year. At current mercury and cadmium concentrations of 2.87 mg/kg and 3.81 mg/kg dry solids respectively, this equates to 1.2 tonnes of mercury and 1.6 tonnes of cadmium passing down this route and being released into incinerator flue gases. Assuming more than 99% arrestment in the gas cleaning system, this quantity of metal is likely to be landfilled unless commercial outlets are found for the ash residues.

14.6.3 On waste water treatment plants with incinerators, it is essential that any scrubber liquors or other liquids in contact with the combustion process are not returned to the sewage stream for treatment. If this happens, the concentration of metals, mercury in particular, increases in the sludge until an equilibrium is achieved with metal losses in the incinerator flue gases (Balogh et al. 1995).

14.7 Sewage Sludge Disposal to Landfill

14.7.1 Landfill of sewage sludge in the UK has decreased; in 1980 in excess of 260,000 dry tonnes were landfilled, in 1991 this had reduced to 115,000 tonnes and then increased slightly to 123,000 dry tonnes in 1994 (DoE 1996). 123,000 tonnes dry sludge is equivalent to around 0.35 tonnes and 0.47 tonnes mercury and cadmium respectively to landfills.

14.8 Conclusions

14.8.1 Waste water treatment plants concentrate mercury and cadmium from dilute solution in domestic sewage into the sludge for subsequent disposal. Conservative wastewater removal efficiency estimates for conventional activated sludge plants are 60% and 70% for mercury and cadmium respectively. Advanced tertiary treatment for solids removal may increase overall removal efficiency further. There are no simple, widely applicable improvements to enhance process metal removal efficiency from the wastewater stream.

14.8.2 In 1994, approximately 3.0 tonnes of mercury and 4.0 tonnes of cadmium were captured into sewage sludge. Most of this was subsequently spread on land.

14.8.3 From the metal removal efficiency figures above, then approximately 5 tonnes of mercury and 6.7 tonnes of cadmium passed preliminary treatment at waste water treatment plants in the UK.

14.8.4 The only practicable means of reducing mercury and cadmium burdens in municipal wastewater is to restrict metal releases to the sewer at source. This has been achieved under IPC for scheduled industrial processes for both metals, but particularly for cadmium which continues to reduce annually in the UK.

14.8.5 The mercury content of sewage seems to have stabilised pending further regulatory action to reduce the mercury inputs further. The obvious mercury source is waste amalgam from dental surgeries, but there is no firm evidence yet that this heavy particulate material is passing preliminary treatment. Mercury leaching from amalgam fillings may be a significant source of mercury particularly in densely populated areas.

14.8.6 The cessation of sewage sludge dumping at sea will increase the metal burden to land and landfill by approximately 50% and 45% for cadmium and mercury respectively

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15. TREATMENT TECHNOLOGIES FOR MERCURY AND CADMIUM IN LIQUID WASTES

15.1 Introduction

15.1.1 In this section we review the commercially available techniques for removing mercury and cadmium from a variety of waste waters. We also briefly address monitoring technologies and report on a limited survey of UK companies supplying small scale end-of-pipe treatment equipment in 1994.

15.1.2 Established end-of-pipe technologies are reviewed in principle and potentially innovative techniques are highlighted. It is not the intention of this study to examine in depth the theory of metal removal from liquids, however we have concentrated on the practical aspects of available technologies where possible.

15.1.3 Mercury and cadmium occur in a variety of industrial liquid discharges as discussed in other sections of this report. Simplistically mercury and cadmium will appear in waste waters from industrial processes where it is not possible to use metal-free raw materials, or where mercury and cadmium are inherent components in product manufacture. Mercury and cadmium contamination also arises from cross media abatement technologies, such as wet gas scrubbing.

15.1.4 Metals may be in solution individually or as a mixture. They may be present as particulate matter, complexes with other ligands or chelating agents.

15.1.5 Liquid discharges containing prescribed substances are regulated by the IPC authority together with the requirements of the sewerage undertakers. Suggested release to water concentrations are given in the IPC Guidance Notes published. In the past cadmium and mercury concentrations in effluent were set based on the EQOs of the receiving waters, rather than the absolute limits specified in EU directives 85/513/EEC, 82/176/EEC and 84/156/EEC of 0.2 mg/l cadmium and 0.05 mg/l for mercury.

15.1.6 In addition to release limits on mercury, cadmium and other prescribed substances, consents to discharge contain a variety of other restrictions and exclusions that impact on the applicability of particular treatment technologies. Sewerage undertaker consents under the Water Industry Act 1991 usually include;

- instantaneous and average flow values;
- permitted pH range (typically 6 to 11);
- limits on all relevant toxic metals;
- limits on sulphide concentration (typically less than 5 mg/l as S);
- temperature not to exceed 43.3 °C;
- other organic chemical exclusions.

15.1.7 The "catch-all" concentrations for release to waters given in early HMIP IPC Guidance Notes were 0.02 mg/l and 0.05 mg/l as mercury and as cadmium respectively. These were monthly, flow weighted, average concentrations, but an absolute limit of twice the monthly average value was suggested. Later Guidance Notes, such as IPR 4/9 for Pharmaceutical Processes, revised the monthly flow weighted average concentration down to 0.005 mg/l and 0.01 mg/l for mercury and cadmium respectively. The absolute limit of twice the monthly average concentration is retained.

15.1.8 The HMIP Guidance Notes for processes involving either cadmium and its compounds (IPR 4/23), or mercury and its compounds (IPR 4/24) set slightly different release levels for water. IPR 4/23 specifies a limit of 0.05 mg/l cadmium and 0.005 mg/l for mercury. IPR 4/24 specifies 0.01 mg/l mercury only.

15.1.9 IPC requires compliance with standards of this quality for new processes, but existing inorganic chemical processes were required to submit IPC authorizations August 1994. The chlor-alkali industry are classified as processes involving halogens which applied for process authorization before 31 January 1994.

15.1.10 Each waste must be considered individually with regard to the suitability of pollution control processes due to the complexity of the reactions between components of the mixture. The treatment processes described are not necessarily unique to mercury or cadmium removal and can be expected to remove a range of pollutants including other toxic metals.

15.1.11 Mercury and cadmium can be present in a variety of chemical forms in the effluent produced from the industrial processes depending on the source and nature of the effluent. The metals may be present as sparingly soluble solids, in solution or complexes with other ligands or chelating agents.

15.1.12 Treatment technologies described in this text refer to removing metal cations from solution. Techniques for removing organo-mercury compounds present in trace quantities tend to be dominated by biological or chemical adsorption methods, ion exchange and wet oxidation techniques.

15.1.13 Although critical to the satisfactory performance of an end-of-pipe treatment process, basic process engineering requirements, for example pre-treatment such as pH control, cyanide destruction and load buffering, or precautionary measures, such as bunding, are not discussed in detail. This appraisal concentrates on the fundamental metal removal technology.

15.1.14 The BAT principles, given in IPRs 4/23 and 4/24, applicable to treatment technologies are acknowledged, but not discussed in detailed here unless pertinent.

With respect to electroplating in particular, BAT is expected to include;

- separation and treatment of cadmium or mercury waste streams from other process wastes;
- waste minimisation and waste reduction within the process design and operation;
- effluent volume minimisation; dilution is not acceptable to meet concentration based limits. This implies that treated effluent should be recycled to the process or re-used elsewhere for less exacting processes;
- consideration of recycling metals within the process to avoid release to any environmental medium, a so called zero release strategy. In reality few processes recover metal in a form where it can be directly re-used within a process, therefore the metals removed from the liquid waste are either recovered as scrap, or deposited in landfill as solid residues.

15.1.15 To achieve high quality effluent, flow equalisation capacity is essential to minimise fluctuations in flows and loads. Installation of additional treatment stages, such as anion exchange or evaporation, produces high quality effluent suitable for re-use, thereby minimising water consumption costs and effluent volume.

15.1.16 BAT includes waste and effluent minimisation among primary objectives. In electroplating operations the following waste minimisation options can be considered (USEPA 1988);

- reduce dragout from plating tanks by:
    - i) proper positioning of workpieces on plating racks;
    - ii) increasing plating solution temperatures;
    - iii) lowering plating solution concentrations;
    - iv) install drain boards to increase dragout recovery.
- extend plating bath life by:
    - i) reducing drag-in by improved rinsing;
    - ii) using demineralised water as make-up water;
    - iii) using purer anodes;
    - iv) returning spent solutions to supplier.
- reduce the rinse water volume by:
    - i) using multiple countercurrent rinse tanks;
    - ii) using spray or fog rinsing.
- prevent dust from adjacent buffing or polishing from entering the plating room and contaminating plating baths.

There are large operating and capital cost savings and effluent volume reductions achievable by optimising rinsing techniques. For example, during manual plating of aircraft pieces, the rinse water required in a single static bath is 1,600 litres per m^2 compared to 16 and 3.5 litres per m^2 for 2 and 3 stage cascade rinses (UNEP).

15.1.17 In cadmium electroplating lines, all stages tend to be contaminated by cadmium with time, including degreasing and rinsing prior to plating, and passivation and stripping stages post plating. Therefore collection and treatment of effluent from all treatment stages must be considered in IPC.

15.1.18 The liquid discharge concentrations suggested for mercury and cadmium represent those for the best available technology. It is unlikely that the current release limits can be achieved by a single process step, and therefore two or more processes, in addition to pre-treatment, are usually used; for example a bulk cation removal stage followed by a polishing or scavenging stage to achieve the required concentrations.

15.1.19 The basic objective of all end-of-pipe metal removal processes is to separate and concentrate metals from dilute solutions. Concentrated metal bearing streams can then be economically treated and disposed of, usually as solid residues to landfill. Liquid metal bearing wastes are typically treated by hazardous waste contractors using precipitation and immobilisation techniques. If the concentrated stream from a treatment process is suitable, metals can be recovered using electrochemical or other hydrometallurgical techniques.

15.1.20 The established technologies for treating metal-containing waste waters are;

- chemical precipitation using one or more of the following inorganic reagents calcium hydroxide, sodium hydroxide, sulphides, sodium carbonate, magnesium hydroxide, or an organic precipitant such as TMT 15. A solids separation step then follows;
- ion exchange in which metal ions are removed onto a synthetic organic resin or natural inorganic material. The metal saturated exchanger is regenerated to elute the metal in a relatively concentrated form for further treatment. A range of ion exchange materials are available and efficacy varies from waste to waste. Generally chelating synthetic resins are most effective for mercury and cadmium containing wastes;
- electrochemistry where metal ions are plated onto a cathode for reuse or disposal. A variety of electrolytic cells are available;
- membrane processes operating at the molecular level, such as reverse osmosis or electrodialysis, or solids removal methods such as microfiltration and ultrafiltration. Membrane processes are available in a variety of different process configurations;
- co-precipitation combining conventional precipitation with flocculation/coagulation chemistry. The precipitating metal complexes adsorb onto the growing flocs and achieve residual metal concentrations below the solubility level of the precipitating system;

Other processes including patented processes, chemical reduction, carbon adsorption, and bio-accumulation/adsorption.

15.1.21 Currently we understand BAT applicable to cadmium electroplaters to be stream segregation, the use of electrochemical cells to minimise dragout rinse losses, followed by cation exchange. Effluent from the cation exchanger is discharged to sewer, or treated by anion exchange to allow reuse for process purposes. Cation regenerant is treated by a further electrochemical cell to recover cadmium as anode material, or is removed by hazardous waste contractors for disposal. There are variations on this scheme involving the omission of the electrochemical cells and the batch treatment of regenerant liquors using organic precipitator materials. Solid waste, spent exchanger materials or small quantities of liquid wastes are disposed of by hazardous waste contractors.

15.1.22 The attraction of using electrochemical cells is emission control and recovery of metal to offset costs, however, the relatively low cost of replacement electroplating solutions means long payback periods for this technology. Greater cost savings probably arise from savings in water consumption.

15.1.23 There are various innovative techniques for metals removal that are not widely established in the UK, or exist at research or pilot scale only. As with many innovative processes, only a small number will become accepted as robust and economic in general industrial situations. Potential processes which may become adopted are;

- adsorption and/or bio-accumulation using biomass preparations to selectively concentrate metals from solution. This also includes more widespread use of simple technologies such as reed beds. This technology is intermediate between established and developing and so is included in both categories;

- liquid/liquid extraction using impregnated resins which exhibit increased metal selectivity over conventional ion exchangers. Low exchange capacities and loss of activity with time are problems with these materials;

- developments of conventional ion exchanger systems, such as continuous contactors and short bed designs to enhance performance;

- advanced membrane techniques using electrically enhanced filtration techniques, improved membrane cleaning technology, electro-osmotic dewatering of slurries (MacDonald 1991);

- advanced electrolysis cells and rotating electrode systems (MacDonald 1991). Electrochemical cells with very high surface areas are able to remove metals from solution to concentrations suitable for release although there may be problems in regenerating the cathode;

- enhanced ion-exchange technology including electrochemical enhancement of conventional ion exchange systems (MacDonald 1991). Electrochemical Ion Exchange is where an ion exchange material is incorporated into a electrode and ion exchange is controlled by application of an electric current;

- Bacterial Sulphate Reduction has been identified as a potentially valuable process for removing metals such as cadmium, iron, nickel and zinc from contaminated waste waters. Under anaerobic conditions sulphate-reducing bacteria oxidize simple organic compounds with sulphate to generate H_2S which then reacts with metals to remove them from solution as insoluble metal sulphides. Experimental work has shown that such anaerobic reactors were capable of lowering concentrations of cadmium by more than 95% and completely neutralising the acidity of metal-contaminated waters(Dvorak 1992) . However, this work is very much at the experimental stage, and much more work is required to assess the feasibility of such processes for industrial use;

- Biological Sulphide Generation. Other work has been carried out combining sulphide precipitation using sulphide-reducing bacteria, and biosorption to scavenge metal ions from aqueous effluent. High concentrations of sulphide ions near the cell surface allow metal sulphides to be precipitated on the cell wall, and removal is possible using a high grade magnetic separator if the ions are magnetic. The levels to which heavy metal ion concentrations can be reduced are very low - for mercury, a level of 8.02×10^{-46} g/l has been achieved (Watson 1988). Again, this is a novel, experimental technique with unknown potential industrial application.

15.1.24 The choice of economically feasible techniques changes with the scale of operation. For small electroplating businesses hydroxide precipitation technology has historically been the favoured process utilised on the basis of simplicity and low cost when compared to other technologies. For larger operations such as the chlor-alkali brine purification, advanced chemical and membrane processes have been utilised. Ion exchange is capable of achieving high effluent quality standards often as part of a multi-stage chemical and physical separation process. For very large scale operations such as zinc smelting, precipitation and flocculation technology, combined with long retention times in lagoons, are typically used. The commonly established removal techniques are reviewed in the following sections.

15.2 Chemical Precipitation

15.2.1 Chemical precipitation is the most widely used technique for the removal of toxic metals from dilute waste waters. The fundamental principle of chemical precipitation is that most metal cations form insoluble or partially soluble forms with reagent anions in aqueous solution at characteristic pH values. Most metal cations are precipitated by the addition of an alkaline reagent. A precipitant chemical, such as caustic soda (NaOH), lime (CaOH), sodium sulphide, ferrous sulphide, sodium borohydride or organic reagent, such as trimercapto-s-triazine (proprietary brand name is TMT-15) or equivalent, is added to the aqueous waste in a stirred treatment tank. A solids separation phase then follows.

15.2.2 Separation of the metal containing floc has been achieved traditionally by simple gravity settlement often in the presence of flocculation or coagulation aids. However, metal flocs tend to be difficult to separate efficiently, therefore tertiary treatment such as sand filters, candle filters or membrane treatment may be employed to remove fine metal containing solids and meet high quality limits.

15.2.3 The main factors influencing efficacy of any precipitation process are:

- solids separation efficiency; simple gravity settlement is unlikely to be sufficient for a high quality effluent due to the presence of fine metalliferous particles in the effluent stream. Settlement aids, such as polyelectrolytes, or advanced physical separation technology can be used, such as microfiltration or lamellar settlement;

- the solubility of the precipitate formed. Generally the solubility of precipitated material decreases according to the anion as follows:

  carbonate>hydroxide>sulphide

  The TMT 15/metal complex is said to approach or exceed the sulphide solubility values for mercury and cadmium (Personal communication Degussa).

  A comparison of solubility products is given in Table 15.1.

- the presence of stable complexes or chelating agents such as EDTA increases the solubility of the precipitate and may require pretreatment;

- chemical interferences. Competing cations, ionic strength, amphoteric behaviour and pH all affect the efficacy of precipitation and separation.

The net effect of all these factors combined synergistically is that the guidance note concentrations for cadmium and mercury cannot be reliably achieved by precipitation and gravity separation alone. A precipitation system with an enhanced solids removal process can achieve the guidance concentrations.

Table 15.1 - Solubility Products for Mercury and Cadmium

Salt	Mercury (II) Ks	Cadmium (II) Ks
Carbonate	-	6.18×10^{-12}
Hydroxide	1.7×10^{-26} **	5.27×10^{-15}
Sulphide	6.44×10^{-53}	1.40×10^{-29}
TMT 15*	1.4×10^{-47}	7.7×10^{-33}

Sources - Handbook of Chemistry & Physics 70th Edition
* - Degussa Chemicals
** - as oxide

15.3 Hydroxide Precipitation

15.3.1 This is the most common process used to remove cadmium from aqueous streams. The reaction is:

$$Cd^{2+} + 2Na(OH) \text{ --> } Cd(OH)_2 + 2Na^+$$

The hydroxide solubility varies with pH and optimum conditions are essential for effective cadmium removal, which is pH 11-11.5 (if there is a mixture of metals present in the stream, pH 9-9.5 is regarded as optimum for overall metal precipitation). After sedimentation, the typical concentration of cadmium in effluent discharge is 0.5 mg/l (Patterson 1985).

or for mercury removal, it is mercuric oxide which is precipitated:

$$Hg^{2+} + Ca(OH)_2 \text{ --> } HgO + Ca^{2+} + H_2O$$

The solubility of the mercuric oxide is not so pH dependent.

15.3.2 Calcium hydroxide flocs are often gelatinous and difficult to settle and dewater. Magnesium hydroxide has recently become more commercially available for effluent treatment. Magnesium hydroxide reagent offers hydroxide solubilities, but with improved settling characteristics and other advantages associated with pH buffering and eliminating the risk of extreme pH values associated with reagent overdosing.

15.3.3 Hydroxide precipitation on its own is not capable of achieving the mercury and cadmium discharge limits and further treatment is required (HMIP 1993). When sulphide or TMT 15 is added as a scavenging agent, soluble mercury and cadmium concentrations can be less than 0.002 and 0.02 mg/l respectively.

15.4 Sulphide Precipitation

15.4.1 This is more effective than hydroxide precipitation because the resulting sulphides of both mercury and cadmium are much less soluble. The process is used as an alternative to hydroxide precipitation or as a subsequent polishing step. Sulphide is added as readily soluble sodium sulphide, or as sparingly soluble iron sulphide. The reaction for mercury (cadmium undergoes a similar reaction) is:

$$Hg^{2+} + FeS \dashrightarrow HgS + Fe^{2+}$$

In addition, sulphide precipitation shows high metal removal levels even in highly chelated waste waters (ie those containing chelating agents such as EDTA) which can severely hinder hydroxide precipitation.

15.4.2 Care must be taken to maintain pH levels above 8 to avoid the risk of generating hydrogen sulphide (H_2S) gas, and there are difficulties in disposing of the resulting sulphide sludge due to potential sulphide reactivity (Cushnie 1985). Also sewerage undertakers usually impose concentration limitations in trade effluent consents which may require the use of sparingly soluble iron sulphide to prevent overdosing resulting in high effluent sulphide concentrations. If sparingly soluble reagents are used, longer process retention times are required.

15.4.3 A proprietary sulphide precipitation system(Personal communication IonPure) involves pH adjustment to a minimum of 9.5, sodium sulphide addition in a stirred reactor followed by a precipitate ageing tank. The aged solution is pumped through a sorption filter which collects the precipitated solids for disposal. Treated effluent quality claimed is mercury concentrations down to 0.002 mg/l and cadmium down to 0.05 mg/l. Other advantages claimed for the system are the ability to remove metals from chelated solutions and mixed metal solutions and a low sludge generation. The effluent from this plant would not be suitable for reuse without further treatment to remove anions.

15.4.4 More generally, sulphide precipitation followed by filtration has achieved average discharge concentrations of 0.01-0.1 mg/l for cadmium and 0.01-0.05 mg/l for mercury (USEPA 1987). Due to difficulties in removing fine sulphide particles by conventional filtration, sulphide precipitation on its own is unlikely to achieve the guidance release concentrations for new plant (HMIP 1993).

15.5 TMT 15 Precipitation

15.5.1 TMT 15 is liquid organic sulphur containing reagent (trimercapto-s-triazine) marketed as the trisodium salt (Degussa Chemicals). TMT 15 has advantages over most inorganic precipitants as it has low toxicity and is relatively safe to handle, but it is more expensive. TMT 15 precipitates divalent cations, including mercury and cadmium, but not trivalent metals. The solubility product of the mercury precipitate approaches that of mercury sulphide, whereas the cadmium TMT complex is more insoluble than cadmium sulphide.

15.5.2 Due to TMT 15 being more expensive than inorganic precipitant, it is commonly used as a scavenging agent during precipitation treatment in continuous flow plants, or as a single addition to small scale batch treatments. TMT 15 treatment is known to be used in the UK to remove cadmium from ion exchange regeneration liquor, and mercury and cadmium from incinerator gas scrubbing liquors and flue gas desulphurisation plant waste waters.

15.5.3 As with other metal precipitates, metal TMT 15 complexes require physical filtration, such as mixed media filters, and/or the use of sedimentation aids such as polyelectrolytes, to achieve the concentrations permitted for release to the environment.

15.6 Carbonate Precipitation

15.6.1 This has proven to be an effective removal process for cadmium, with precipitation tending to occur at more neutral pH (7.5-8.5) than with hydroxide. The reaction is:

$$Cd^{2+} + Na_2CO_3 \text{ --> } CdCO_3 + 2Na^+$$

The principal advantages are the lower operating pH, and the precipitation of denser, more filterable sludge, but the reaction mechanism proceeds at a slower pace than the hydroxide-based system thus requiring longer residence times (Freeman 1989). Residual solubilities are similar to the hydroxide system.

15.7 Borohydride Precipitation

15.7.1 Sodium borohydride is a reducing agent that is used to precipitate metals from solution as insoluble elemental metal. The process is usually carried out in pH range 8-11 to ensure efficient utilisation of borohydride:

$$4M^{2+} + NaBH_4 + 8OH^- \text{ --> } NaBO_2 + 4M + 6H_2O$$

The process has the principal advantages of producing metal sludge suitable for reclamation, removing metals to lower concentration levels than is possible with conventional treatment, and reported sludge volume reductions of 50%+ over lime precipitation(USEPA 1987). Reported use of sodium borohydride has resulted in mercury levels in waste water being reduced from 10 mg/l to 0.22 mg/l (Patterson 1985). However, borohydride treatment can produce very fine suspended matter which is then difficult to remove, and can also evolve hydrogen gas in acidic conditions. In addition, the high cost of the reagent limits its use in industrial metal contaminated waste waters.

15.7.2 The efficacy of the various precipitation systems under test conditions treating a flue-gas wash water is compared in Table 15.2. In addition to soluble metal concentrations after precipitation, the precipitate was tested for metals content, and a 24 hour elutriation test performed at pH 4. These results are given in Table 15.2, together with the results from other toxic metals.

Table 15.2 - Contents of Heavy Metals from the Precipitation and Elution Experiments

Experiment 0 - Untreated Flue-Gas Wash Water
Experiment 1 - Lime Precipitation
Experiment 2 - Lime and TMT 15 Precipitation
Experiment 3 - Lime and Na_2S Precipitation
Experiment 4 - TMT 15 Precipitation
Experiment 5 - Na_2S Precipitation

Expt No.		Heavy Metal Contents					
	Parameter	**Cd**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
0	Filtrate (mg/l)	1.19	2.81	1.19	0.79	28.5	46.0
1	Filtrate after precipitation (mg/l)	0.13	0.28	0.33	1.0	< 0.45	< 0.02
	sludge, dry (mg/kg),	300	850	1575	100	9165	16650
	eluate (mg/l),	22.2	26.2	2.78	4.2	355	1040
	elution rate (%)	63.9	26.6	1.53	36.3	33.5	53.1
2	Filtrate after precipitation (mg/l)	< 0.02	0.25	< 0.002	0.94	< 0.45	< 0.02
	sludge, dry (mg/kg),	394	971	1107	124	10436	19484
	eluate (mg/l),	25.4	5.0	0.0097	4.5	313	960
	elution rate (%)	71.0	5.67	0.0097	40.0	33.0	54.3
3	Filtrate after precipitation (mg/l)	0.02	0.27	< 0.002	0.97	< 0.45	< 0.02
	sludge, dry (mg/kg),	302	877	1650	112	8970	16525
	eluate (mg/l),	22.6	24.9	0.72	4.7	312	1140
	elution rate (%)	65.0	24.7	0.375	36.5	30.2	59.9
4	Filtrate after precipitation (mg/l)	< 0.02	0.27	< 0.002	0.98	0.45	< 0.02
	sludge, dry (mg/kg),	325	728	1710	108	7830	14440
	eluate (mg/l),	2.7	0.19	0.012	4.4	0.94	885
	elution rate (%)	6.38	0.2	0.0054	31.3	0.92	47.1
5	Filtrate after precipitation (mg/l)	0.02	0.27	< 0.002	1.0	< 0.45	< 0.02
	sludge, dry (mg/kg),	347	773	1780	115	8270	15460
	eluate (mg/l),	27.3	4.1	0.25	0.25	330	980
	elution rate (%)	66.8	4.5	0.12	0.12	33.9	53.8

Source - Paul J. 1988 - reproduced by permission of Degussa Chemicals

15.7.3 The relative precipitation efficiencies and the stability of the resulting sludge are illustrated by these tests. In the case of this waste water; for mercury, both sulphide and TMT 15 with or without lime could achieve the 0.005 mg/l concentration required and produced stable sludge; for cadmium, sulphide and TMT 15 could achieve the guidance concentration of 0.05 mg/l cadmium, but significant leaching of cadmium occurred from the hydroxide and sulphide sludges, but not the TMT 15 sludge.

15.8 Ion Exchange

15.8.1 Ion exchange is commonly used as a polishing process to remove metal cations remaining after the bulk of the cations have been removed by either precipitation or electrochemical techniques. Ion exchange using synthetic resins, usually chelating forms, offer significant advantages in achieving the required standards and being simple and relatively easy to automate. Typically a cation exchange column precedes an anion exchange column allowing a deionised water recycle back to process lines.

15.8.2 Ion exchange systems can adequately treat metal waste streams containing up to about 2500 mg/l (expressed as calcium carbonate equivalent) - above this it becomes prohibitively expensive. The process is generally considered more efficient in treating large flows of dilute hazardous materials than many other processes, and hence is often used following chemical precipitation to polish the effluent prior to final discharge (Alliance Technologies Corporation 1987).

15.8.3 Ion exchange resins are solid insoluble acids or bases which are capable of entering into chemical reactions. Synthetic organic resins predominate today because their characteristics can be tailored to specific applications.

Strong acid cation resins have sulphonic acid groups and exchange cations over the entire pH range, removing a toxic metal by exchanging it for a hydrogen:

$$M^{2+} + 2RH \dashrightarrow R_2M + 2H^+$$

Both mercury and cadmium have high affinities for strong acid cation resins compared to other metals, as shown:

$$Pb > Hg > Ca > Ni > Cd > Cu > Zn > Fe > Mg > Mn$$

Such resins are, however, difficult to regenerate with acid.

15.8.4 Chelating resins contain carboxylic acid groups and regenerate easily with acid. Their principal feature is that they exhibit a high degree of selectivity for mercury - the selectivity coefficient (a quantitative measure of relative preference of a resin for various ions) for mercury is 2800, compared to 12 for cadmium (Waitz 1979). However, the relatively low kinetics of such resins necessitate the use of low flow rates and large resin inventories. In addition they are considerably more expensive than other types and do not function effectively below pH 3-4.

15.8.5 Ion exchange operations are generally carried out in vertical columns in which the resin is fixed, although batch treatment can be effective. Resin is usually regenerated in place where cadmium plating is a continuous operation. Where very small scale intermittent cadmium plating is carried out, resins may be regenerated offsite by specialist contractors.

15.8.6 Various equipment designs exist, usually based on two sets of columns to ensure continuous treatment operation, with switch-over when one reaches exhaustion. Fixed-bed systems normally follow a four step operating pattern (a) exhaustion (b) backwash (c) regeneration (or replacement) (d) rinse. During the exhaustion step the waste solution ions replace the ions bound to the resin until all exchange sites are filled - a condition known as "column breakthrough". If the resin is regenerated (expected only for cadmium) a highly concentrated solution of the ion originally associated with the resin is passed through the bed, and the resulting low-volume brine containing the metal species can be reclaimed by electrochemical methods (Radha Krishnan 1993) or treated chemically.

15.8.7 Ion exchange technology installed in cadmium electroplating shops is reliably achieving guidance concentration limits. For mercury removal, a commercial unit has achieved a final effluent concentration of 0.001 mg/l from an influent of up to 25 mg/l mercury (Patterson 1985).

15.8.8 The performance of a large scale chelating ion exchange process removing mercury from immobilising plant effluent was reported (Ritter et al. 1992). Varying concentrations of mercury (0.2 to 70 mg/l) were reduced consistently to between 0.001 and 0.005 mg/l. Optimum performance of the plant was only achieved after a cartridge filter was installed to remove fine iron particles which adsorbed mercury and passed through the exchange resin untreated, and laboratory waste containing oxidising agents and hydrochloric acid (which formed $HgCl_4^{2-}$ complexes rejected by resin) was excluded.

15.8.9 In summary, for maximum process efficiency the following practical principles apply to ion exchange plant design (Hosea et al. 1988);

- segregation of metal bearing waste streams to enable recovery of individual metals and minimise chemical interference;
- pH control for optimal exchanger performance;
- regeneration should be carried out before metal breakthrough for optimum efficiency,. Breakthrough detection requires on-line detectors which are expensive, therefore elapsed time or volume are normally used to initiate regeneration cycles. Conductivity is not a reliable measurement due to the presence of other ion species;
- most larger systems use dual columns, one duty and one regenerating/standby. Improved efficiency is achieved by using a lead/lag series flow; i.e. lead column is taken offstream for regeneration and then returned to service as the lag column. This system offers the advantages that the effluent stream is given double treatment, the lead column is only regenerated when exhausted and no metal ions escape from process during column changeovers;
- counterflow regeneration is superior to co-flow regeneration as the metal concentration in the regenerate is higher and the regenerated column treats larger volumes of effluent with lower metal leakage.
- substances likely to react or interfere with the ion exchanger should be excluded from the waste water, such as oxidising agents, chlorides and suspended solids.

15.9 Co-precipitation

15.9.1 Co-precipitation is a generic term applied to the addition of coagulants and or flocculants to a precipitating system such that precipitating metals adsorb onto the floc structure. This technique achieves dissolved metal concentrations considerably lower than conventional chemical precipitation alone. The addition of ferric hydroxide, or TiO_2 flocs results in removals in excess of 99% around pH 8 - 10. Commercial co-precipitation systems are available.

15.10 Electrochemical Processes

15.10.1 Electrochemical recovery techniques are based on the oxidation-reduction reaction which takes place at the surface of conductive electrodes immersed in a chemical medium. At the cathode the metal ion is reduced to its elemental form, with gaseous products, such as oxygen or hydrogen, being evolved at the anode.

15.10.2 The attractions of the process are the potential for recovery of metals in a useful form rather than a precipitated sludge requiring disposal, but problems arise when trying to obtain pure metallic product from mixtures of metals from passivation and other treatments. These techniques are difficult to apply to dilute solutions because of the low mass transfer rates, although mass transfer can be enhanced by increasing the effective surface area of the cathode. Hence typical cation concentrations are reduced from around 100-1000 mg/l to 0.1-10 mg/l depending on the cell retention time and interferences. Difficulties may also be encountered if high chloride concentrations are present. Typically electrochemical cells are non-specific bulk removal processes not capable of achieving low concentrations without a subsequent polishing treatment.

15.10.3 The conventional electrochemical reactor consists of the electrodes, a gas venting system, recirculating pumps, and a power supply. After the deposition of metal reaches sufficient thickness (~6mm) the metal can be removed and re-used or sold. Such a reactor is very efficient at high concentration, but not at low concentrations due to the mass transfer-limiting conditions. Conventional UK electrochemical cells use apertures, expanded-metal-mesh electrodes with fluidised glass beads or very high flow rates (i.e. high Reynolds number) to minimise boundary effects and improve deposition (Personal communication Enthone-OMI). The electrodes are regularly removed for metal recovery. Studies have achieved mercury removal from 34 g/l to < 5 g/l (Matlosz et al. 1982).

15.10.4 In cadmium plating applications, electrochemical cells have been installed in many UK companies(Waitz 1979). Typically an electrochemical cell is installed to recover bulk cadmium from rinse waters, followed by ion exchange to remove residual soluble cadmium. Cation exchange acid regenerant is treated in separate small cells to remove cadmium prior to disposal, or alternatively the regenerant is removed by hazardous waste contractors.

The brittle cadmium cathode deposit can be recycled to the plating bath and if an anion exchanger is used downstream from the cation exchanger, then demineralised water can be recycled to the plant approaching zero discharge although the anion exchanger regenerant and cathode deposits may require suitable disposal.

15.10.5 The extended surface electrolysis (ESE) system is a sandwich construction of fibrous steel cathode, separators and screenlike anode rolled into a spiral and inserted into a pipe. A number of cells can be stacked as modules so that a large fraction of metals can be recovered. The mechanism for metal removal from effluent is essentially the same, but this design recovers metal better at low concentrations than at high - i.e. at < 10 mg/l. In the high surface area (HSA) reactor, the cathode achieves a large surface area by incorporating a large number of carbon-filament mats. An *installed* example in Canada is reported to recover 99.9% of the cadmium in the effluent. The major disadvantage with these advanced designs is that the metal cannot be removed from the cathode mechanically. Instead it is usually stripped out by circulating an acidic cleaner through the cell (Campbell et al. 1982)

15.11 Membrane Technology

15.11.1 Advanced membrane processes include microfiltration, ultrafiltration and reverse osmosis. Microfiltration and ultrafiltration are used in combination with chemical treatment for the physical separation of sludge, ie to 'polish' before treated effluent discharge. Reverse osmosis is used to separate a dilute solution into a pure solvent fraction and a residual concentrated solution.

Microfiltration and Ultrafiltration

15.11.2 A typical treatment system involves chemical precipitation followed by pressurised feed of the underflow through a semi-permeable membrane to remove the precipitated solids. The concentrated stream produced by these processes is chemically different to the process i.e. plating, solutions and therefore cannot be recycled directly.

15.11.3 Cartridge microfiltration and cross-flow ultrafiltration remove particulate material from effluent treated by precipitation techniques. Membrane processes offer superior performance to conventional sand filtration techniques as much finer particulate material can be removed (including colloidal material), blinding is much less of a problem, and acceptable throughput can be obtained even with very fine ultrafilter membranes.

15.11.4 Cartridge microfiltration collects solid material for disposal. Cross flow microfiltration and ultrafiltration produce a concentrated metal bearing liquid or slurry for disposal as for cartridge microfiltration. These techniques may be applied on a continuous or batch basis.

15.11.5 There are a variety of membranes available including textiles, ceramic, organic and inorganic materials; other materials may be included in the membrane structure to enhance performance. The membrane retains materials based solely on size, shape and molecule flexibility, acting as a sieve to retain dissolved and suspended materials that are physically too large to pass through its pores. The retained material (concentrate) then leaves the process separately from the purified solvent.

15.11.6 Membranes are composed of a thin (0.1-1 μm), selective, surface layer supported by a porous, spongy layer about 100 μm thick. Ultrafilter and microfilter pore sizes range from around 0.005 to 10 μm. They can be made from a variety of materials such as cellulose acetate, polysulphone, polycarbonate, PTFE, PVC, sintered glass, and alumina, so it should be possible to obtain membranes that are capable of withstanding most chemical environments that arise in liquid waste treatment.

15.11.7 Several configurations are available that differ in cost, membrane area/volume ratio, and resistance to fouling. Tubular modules are the simplest design in which feed is pumped along the internal bore at a pressure of several atmospheres. Low molecular weight solutes and water permeate the membrane and collect in the outer casing, whilst reject material continues to flow through the tube and is removed at the other end of the module.

15.11.8 Operational precipitation/ultrafiltration performance has achieved a cadmium treated effluent concentration of 0.05 mg/l from an influent of 28.2 mg/l, and a mercury treated effluent of 0.07 mg/l from 15 mg/l (Sternberg et al. 1987). Other textile cross-flow processes achieved cadmium concentrations as low as 0.01 mg/l (depending on the precipitating reagents used), but mercury concentrations tended to be in excess of 0.05 mg/l although this will depend on the precipitating chemicals used (Personal communication Exxflow).

Reverse Osmosis

15.11.9 The major industrial application of reverse osmosis at present is desalination, but it is used in the metal finishing industry, and research is ongoing into its applicability for the treatment of other metal-contaminated industrial waste waters.

During the process, pressure is applied to the more concentrated solution to reverse the normal osmotic flow, and pure water is forced through a semi-permeable membrane into a less concentrated solution by operating at about 5-15 times equilibrium osmotic pressure. Thus a dilute solution can be separated into a pure solvent fraction and a residual concentrated solution. The main advantage is that often both the recovered solvent and the concentrated solute can be recycled or reclaimed.

15.11.10 The semi-permeable membrane requires a high water permeability and low salt permeability, and the three most commonly used materials are cellulose acetate, aromatic polyamides and thin-film composites (consisting of a thin film of a salt-rejecting membrane on the surface of a porous support polymer). Various modular designs are available and the performance is a function of the membrane type, dissolved solids concentration, feed temperature and applied pressure.

15.11.11 Reverse osmosis is used in the metal finishing industry especially for nickel recovery (mainly in the USA). The advantage of this technique is that the metal is recovered unchanged and can therefore be recycled back to the plating plant resulting in cost savings and realistic payback periods.

15.11.12 Reverse osmosis for treating nickel, cadmium and chromium was evaluated using spiral wrap and thin film composite membranes after ultrafiltration treatment(Schoemann et al. 1992). Results were reported as 97% water recovery and cadmium was reduced from 590 to 2 mg/l. Treating a mixed electroplating effluent, cadmium concentration was reduced from 10.1 to 0.4 mg/l. Membrane fouling was a problem treating the cadmium rinse water although not with the other metal rinse waters. On the basis of these results, it seems unlikely that reverse osmosis in isolation will achieve the guidance concentration of 0.05 mg/l cadmium in electroplating rinse waters, but would have value for bulk metal removal for recycling.

15.11.13 Despite the apparent process advantages of membrane techniques, reverse osmosis technology uptake in the UK has been low except for high value, low volume separations. This can be attributed to high capital and operating costs compared to other technologies, membrane fouling and possibly suspicions in industry with respect to complexity, robustness and reliability.

15.11.14 Cartridge and cross-flow techniques have been introduced as polishing processes after precipitation stages. The metal concentration of the permeate produced will depend on the precipitation chemicals used. One manufacturer supplies batch cartridge filtration systems to remove metal precipitates from cation exchanger regenerate liquors which consists of adding a precipitating agent (TMT 15) to a regenerant solution and recirculating the solution through a microfiltration cartridge filter until the dissolved metal concentration is low enough for discharge or re-use.

15.12 Other Processes - Patented Processes

15.12.1 In addition to conventional process technologies, there are various patented processes available for metals removal such as the Andco process and the IMAC-TMR process for mercury removal. These are typically used in large scale chemical plants.

15.12.2 Large scale cadmium and mercury removals have been traditionally carried out at smelting plants. Stringent effluent standards are achieved by separating low contamination streams from high concentration streams. Metals in solution are precipitated under controlled pH in the presence of polyelectrolytes and gravity separation employed. Effluent standards of 0.07 mg/l for cadmium and <0.008 mg/l for mercury are reported for a Belgium smelter (Vanhecke 1992). If volumes of contaminated water are excessive, solids separation in high retention time lagoons or equivalent is typical.

15.13 Chemical Reduction

15.13.1 Chemical oxidation-reduction reactions are those in which the oxidation state of one reactant is increased and the oxidation state of another reduced. Although in such reactions metal ions receive electrons and thus are reduced to an elemental state suitable for recovery, this type of process has found only limited application.

Essentially the process requires the mixing of two aqueous liquids, either on a batch or continuous basis. Reaction rates may be increased by increasing temperature, but this is balanced by increased capital and operating costs. There are a number of reduction reagents available, including zinc, aluminum, iron, hydrazine, formaldehyde, formic acid, sodium borohydride and sodium hypophosphite.

15.13.2 Sodium borohydride use is increasing as environmental concerns and regulations require more complete removal of metals. The reaction involves 1 mol NaBH4 replacing 4 mols of divalent metal ion. The theoretical weight ratio of metal reduced per weight of reagent (ie maximum kg of metal reduced per kg of NaBH4) is 21 for Hg^{2+} and 12 for Cd^{2+} (USEPA 1987).

The use of zinc results in an reaction between the metal and the zinc to form a solid amalgam. This is removed from the aqueous stream and sent to landfill. It is known that this process has been used to treat mercury-contaminated effluent by at least one UK chlor-alkali manufacturer.

Oxidation/reduction treatment tends to be most suitable for low concentrations (< 1%) in wastes, and increased use of this type of treatment technique could increase in the future (USEPA 1987).

15.14 Carbon Adsorption

15.14.1 Activated carbon adsorption can be used to remove a wide variety of contaminants from aqueous streams. The carbon itself is available in either powder or granular form. The granular form is more convenient for use in conventional unit processes and regeneration equipment, whereas the powdered form offers higher surface area and maximum rate for sorption of contaminants. Activated carbon has a fixed adsorption capacity for each type of metallic compound, and once this capacity is saturated, contaminants will no longer be adsorbed and the carbon must be regenerated or replaced. Regeneration can be achieved by using a strong acid or base to remove the metal particles and bring them back into solution.

15.14.2 The main parameters that influence the metals removal efficiency of activated carbon are the specific surface area, pore structure, surface chemistry, pH, temperature, metal concentration and ionic strength. Chelating agents such as EDTA and NTA significantly increase the removal of mercury and cadmium by carbon material (Personal communication Degussa).

15.14.3 The actual process of metals removal often involves the use of multiple columns filled with carbon and operated in series or parallel configurations. Carbon depth should be high enough to remove all the metals from the solution down to the required concentration. Columns are operated in two basic modes - in the fixed bed mode all of the carbon is replaced with fresh/regenerated material when contaminant breakthrough occurs; in the moving/pulse mode only that portion of the carbon that has been exhausted is removed and replaced.

15.14.4 Adsorption is based on the principles of attractive (van der Waal's) forces that exist between metal ions and activated carbon sources. In general the process requires that the metal ion concentration in the waste water stream is less than 1000 mg/l and preferably less than 500 mg/l. Regeneration can be achieved by using a strong acid or base to dissolve and wash the metal particles from the pores and surfaces of the carbon. The metal may theoretically then be recovered by electrochemical techniques, although no information is available regarding any such combination of systems being used for metal recovery. If the carbon adsorption system is not employed for metal recovery for recycling (or when carbon use is low, as carbon re-use is not cost-effective in such a situation), other techniques are used, such as thermal regeneration, incineration, crushing and shredding.

15.14.5 Although there has been limited application of activated carbon use in metals removal, and information from pilot studies etc is scarce, what results are available from studies on metal-contaminated wastes indicate that;

- carbon adsorption capacity increases with chelation of mercury and cadmium in solution;
- reduction of mercury ions to the elemental state may continue even after their adsorption onto carbon;
- sulphurising agents increase mercury removal from waste streams;
- low pH increases adsorption onto carbon, and hence high pH may facilitate regeneration.

15.14.6 Activated carbon adsorption is really only practical for treatment of waste water with a low metal concentration. Hence its principal potential use is as a polishing step following heavy metal precipitation. It is particularly significant after sulphide precipitation because of its ability to substantially reduce residual sulphide concentration, thereby lessening the potential for H_2S gas evolution and the concern for sulphide toxicity (Ku et al. 1987).

15.15 Bio-adsorption/Bio-accumulation

15.15.1 Considerable research has been directed at the removal of ions from solution by living or dead biomass. Biomass used in waste water treatment plant tends to concentrate heavy metals has been known for some time - this removal and concentration capacity has caused concern when considering treatment alternatives for sludge disposal to land. However, work on such biological processes for the removal of heavy metals from industrial waste streams has shown that they can provide attractive, and possibly more economical, alternatives to the commonly used physico-chemical processes (Lowe et al. 1987). High removal efficiencies sufficient to meet the guidance standards have been achieved at pilot or small scale. Preparations are commercially available in the UK to concentrate heavy metals followed by acid regeneration to elute the adsorbed metals. Such preparations are alleged to be stable for over 100 cycles.

15.15.2 Reed beds or equivalent techniques have been used to treat soluble metal containing wastes from road runoff, mining, coke production and chemical manufacture. Metals may be precipitated within the medium by sulphide, or alternatively may be actively taken up by the reeds allowing harvesting. This technique has not been installed for treatment of metal plating wastes to our knowledge. The long term aspects of saturating an ecosystem on a large scale with toxic metals may be questionable especially if the hydraulic transmission of the reed bed declines with time such that excavation and replacement are necessary. Also, accumulated metals that become immobilised as sulphide could be released if the strata becomes aerobic. The disposal route for contaminated biomass/bed medium is unclear, but will depend on the degree of contamination.

15.16 Biosorption

15.16.1 Biosorption, used as a final polishing process, appears to have the greatest immediate potential for use in treatment of cadmium and mercury waste waters. Microorganisms, including actinomycetes, bacteria, algae, fungi and yeasts have the ability to accumulate heavy metals from their external environment. Both living and dead cells are capable of accumulation, but in general the use of dead biomass is favoured because the need for expensive maintenance of living cultures is eliminated and metal recovery/biosorbent regeneration can be optimised without concern about effect on living cells.

15.16.2 For dead cells, surface binding (biosorption) is the main mechanism as the wall of bacteria, algae, fungi and yeasts are efficient metal biosorbents. Initial binding may be followed by inorganic deposition of increased amounts of metal, up to 50% of dry weight. Ionic and covalent bonding may be involved in biosorption with bacteria, whilst physico-chemical interactions seem to comprise the majority of binding in algal cell walls, and a variety of ligands involved in biosorption to fungi and yeast cell walls. Pilot plant studies using bacteria showed an overall cadmium retention within a biological system of 95% from an influent of 1 mg/l (Waitz 1979).

15.16.3 Industrial applications of biological processes for metal removal depend on the ease of metal recovery. Biosorption onto cell surfaces is often easily and effectively reversible by simple means such as use of acid or carbonate solutions.

15.17 Sludge Disposal

15.17.1 The principal problem of most treatment techniques is that the metal contamination is generally simply transferred from aqueous waste to solid waste. The sludge generated still require further treatment and/or disposal. For most metals, the most common method is dewatering of the sludge by pressure or vacuum filtration (to 15-20% solids), followed by disposal of the sludge cake either in hazardous waste landfill or co-disposal with municipal solid waste.

15.17.2 There are also various techniques available designed for recovery and re-use of the metals in the sludge (particularly mercury), but the economics of such processes are poor. Chemical fixation is intended to improve landfill disposal by chemically and/or physically binding and retaining wastes within a matrix, and hence only permitting very slow release of toxic compounds.

15.18 Metal Detection and Monitoring

15.18.1 Historically cadmium and mercury analyses in the parts per billion range have been expensive laboratory operations using atomic absorption spectroscopy, HPLC or equivalent techniques on individual samples. Online monitoring was not usually practicable for small scale activities using these techniques, although cold vapour mercury monitoring could be used.

15.18.2 More recently Anodic Stripping Voltammetry (ASV), as used for detection of trace metal concentrations particularly in saline waters, has been adapted for online monitors. ASV monitors are typically capable of measuring mercury concentrations in the range 0.005 to 100 mg/l and cadmium concentrations in the range 0.001 mg/l to 100 mg/l depending on interfering substances present. Fixed site semi-continuous monitors have been available for several years, however they have tended to be expensive approaching £50,000. More recently the need to measure mercury, cadmium and other toxic metals at concentrations below 0.1 mg/l has resulted in the availability of cheaper online monitors and portable monitors costing less than £10,000. For some metals, portable ASV monitors are available for around £1,500 although not for cadmium or mercury at present.

15.18.3 The rapid development of ASV monitors to measure trace metal concentrations is enabling companies using mercury and cadmium to perform rapid, simple spot measurements when necessary thus allowing optimisation of treatment facilities.

15.18.4 Companies known to offer onsite monitoring capable of detecting trace quantities of mercury and cadmium are;

Supplier	Online Monitor	Portable Monitor
Ionics UK	ASV - incl. Hg & Cd	-
Sartec	ASV - incl Hg & Cd	ASV incl Hg & Cd
Seefelder's Hg-MAT analyser (Windsor Scientific Ltd)	Hg only	-
Palintest	-	ASV for Cu & Pb

15.19 Mercury and Cadmium Removal - Company Capability Survey

15.19.1 A non-exhaustive telephone survey was undertaken in 1994 to identify UK companies offering suitable technology to remove mercury and cadmium from waste waters particularly small and medium size turnkey plants. Of some 39 companies contacted, 13 companies can or would like to supply equipment for removing cadmium from waste waters; 9 companies can or would like to supply equipment for removing mercury from waste waters. The company details are shown in Table 15.3.

15.19.2 Companies identified as supplying mercury and cadmium removal technology were asked for budget capital and operating costs for the technology they supplied. However, few replies have been received probably due to the difficulties of supplying general costs when individual plants are tailored for specific applications.

Table 15.3 - LIST OF COMPANIES CONTACTED REGARDING MERCURY AND CADMIUM REMOVAL TECHNOLOGY FROM WASTE WATER 1994

Company	Telephone No.	Cadmium Removal	Mercury Removal
BEWT	01789 763669	✓	✓
ETA Process Plant	01889 576501	X	X
Yorkshire Environmental Effluent and Water Treatment	01709 841001	X	X
Gee and Co.	0121 359 0212	✓	?
Satec	01270 584011	X	X
Biomechanics Environmental	01902 791616	✓	?
OSC Process Engineering	0161 428 0747	X	X
Simon Hartley	01782 202300	X	X
PWT	0181 560 5199	?	?
ERG Lancy	01403 271711	✓	✓
Degussa	0161 486 6211	X (not UK)	X (not UK)
Water Engineering	01295 810581	X	X
Jones and Attwood	01384 392181	X	X
EWS	01373 858090	X	X
Renovexx Technology	01388 420181	✓	✓
Lurgi	01483 730044	X	X
Invent Water Treatment	01706 359155	X	X
Denver Process Engineer	01372 379313	X	X
Wyatt Ltd	01691 662592	X	X
Yorkshire Metal Fabrication	01532 434311	X	X
ACWA Services Ltd	01756 794794	X	X
Haden Drysys Environmental	0121 765 4040	X	X
Wemco GB	01788 546767	X	X
Aquatec	01942 603268	✓	
Birwelco	0121 550 4777	X	X
Environ	01204 24262	X	X
Environmental Engineering	01775 768964	✓	✓
Rodway and Taylor	0121 236 4027	X	X
Dewplan	01494 535671	X	X

Company	**Telephone No.**	**Cadmium Removal**	**Mercury Removal**
Euthone - OMI	01483 715971	✓	X
Ionpure	01992 501513	✓	✓
BTR Industries	0171 834 3848	X	X
Cirquip	01926 484 378	X	X
Effluent Treatment Systems	01604 740006	✓	
Engineering Services for Plating	0121 59 8061	X	X
PMD Engineering	01203 466691	X	X
Thompson Kennicott	01902 753353	✓	✓
Memcor	0162 982 3811	✓	✓
Biwater	01706 367555	X	X

Key:

✓ = Company supply technology and have established UK record.
x = Company does not supply technology or subcontracts to others.
? = Company will supply technology if requested, no UK installations

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16. BEHAVIOUR OF MERCURY AND CADMIUM IN SOILS

In this section, we review the behaviour of mercury and cadmium in soils. Mercury and cadmium are added to arable land in sewage sludges and fertilisers and to all land by atmospheric deposition. Mercury addition as in pesticides and fungicides was banned in 1992. The metal burden added to the soil is either immobilised in the soil structure, leached into surface or ground waters, taken up by vegetation, metabolised by soil microorganisms or in the case of mercury, evaporated. There is therefore a risk of contamination of the hydrosphere; this aspect is reviewed.

16.1 General Soil Composition

16.1.1 Soil consists of four main components in varying proportions, the relative amounts of which determine the soil's suitability for activities such as agriculture. Typical values for a silt loam surface soil in ideal condition for plant growth are: inorganic fraction 45%, normally composed of small rock fragments and minerals of various kinds; organic matter content 5%, composed of accumulated plant and animal debris; and air and water content each varying between 20-30% (Brady 1984).

16.2 Factors Influencing the Availability of Heavy Metals

16.2.1 The solubility of heavy metals in soils determines their mobility in the environment and their availability to plants as they must be present in solution around the root hairs for uptake to occur. Various soil properties influence solubility, these include; pH value, redox potential, texture, mineral composition (content of clays and oxides of iron and manganese), cation exchange capacity, amount and type of organic compounds present, presence of other heavy metals, soil temperature, moisture content and other factors which affect microbial activity (Harmsen 1977).

16.3 Cadmium in Soils

16.3.1 A trend of increasing soil cadmium concentration has been seen in EU countries and there is evidence that the increase has been greater over the last 20-30 years (OECD 1993), principally as a result of atmospheric deposition, cadmium-containing fertilisers and sewage sludge application. Increasing exposure to cadmium through the consumption of food crops, livestock and contaminated ground water is considered to be the most relevant critical pathway for increased human exposure (OECD 1993). The relative contributions of cadmium to soil from these three major anthropogenic sources in western countries have been estimated at:

- phosphatic fertilisers:	54-58%
- atmospheric deposition:	39-41%
- sewage sludge:	2-5% (Yost & Miles, 1979).

16.3.2 The source of the cadmium is important in determining its availability. Input from atmospheric deposition is more soluble, and thus more available for plant uptake than that derived from say mining activities which tends to be in the form of mineral matter (Hutton 1982).

16.3.3 Estimates of the half-life of cadmium in soils vary between 15 and 1100 years (Kabata-Pendias et al. 1984) and so the potential exists for very long-term accumulation. It is therefore crucial to identify mechanisms and conditions involved in the mobilisation of cadmium in the soil and, if possible, to ensure that these conditions do not occur.

16.3.4 Cadmium concentrations in the majority of EU agricultural soils probably lie within the range; 0.1-2μg/g with most values being less than 1.0μg/g (Hutton 1982). Concentrations in surface soils of background areas are typically in the range 0.1-0.4μg/g (WHO 1992). Values for land recognised as being contaminated are, in general, between 6-97μg/g although a value of 800μg/g has been recorded at Shipham in Somerset (OECD 1993). A survey of 2276 soil samples from England and Wales gave a mean cadmium content of 1.2μg/g and a median of 0.9μg/g. Some of these soils had been contaminated in some way, possibly by sewage sludge or fertiliser application, as values as high as 114μg/g were recorded (MGrath 1986).

16.3.5 Plants vary widely in their ability to take-up and accumulate cadmium with members of the lettuce and beet families having the highest measured levels (Davis et al. 1980).

16.4 Effect of pH on Cadmium Concentration

16.4.1 The principal mechanism by which availability is reduced is by adsorption onto the surface of various components, mainly clays and organics, which results in the formation of large, insoluble complexes. Cadmium adsorption can be greatly enhanced by increasing the pH of the soil: adsorption increased by a factor of three for every pH unit increase between pH4 and 7.7 on sandy and loamy soils (Christensen 1984). This is partly due to a lack of suitable adsorption sites on the surface of soil constituents at low pH. Soil from Shipham was found to have a lower concentration of cadmium in solution than many other soils, this was attributed to the high pH (7.7) and high calcium carbonate and hydrous oxide contents of the soil (Alloway et al. 1988).

16.4.2 Desorption experiments have indicated that sorption is almost completely reversible and so, whilst a soil may have a significant capacity to sorb cadmium, it cannot be considered a permanent sink (Christensen 1984).

16.4.3 When cadmium is added to neutral soils as a soluble compound, more than 70% is likely to be available for plant uptake, 2-3% is expected to remain in solution, 50% bound weakly to clay minerals and 30% bound to organics. A considerable fraction of that bound to organics will remain available for plant uptake. In alkaline soils a significant amount will be precipitated as sparingly soluble compounds and about 10-15% of the total will remain available. In acidic, anoxic and poorly drained soils the mobility and availability will be considerable and probably modified by the amount of microbiological activity occurring (Coughtrey et al. 1983).

16.5 Addition of Calcium Carbonate

16.5.1 The standard mechanism for reducing bioavailability of cadmium in soils is liming (i.e. addition of $CaCO_3$) which has a high affinity for cadmium (Alloway *et al.*, 1988). However, one study reported that liming caused an increase in cadmium content in radish leaves when the addition of the $CaCO_3$ caused an increase in pH to alkaline conditions (Davies et al. 1984). It would therefore be erroneous to assume that maximal amounts of adsorption will occur merely because a soil is neutral or alkaline: in soils rich in other metals such as Cu, Ca, Zn, competition for adsorption sites will occur and so cadmium can remain in solution at high pH values. Thus, pH is just one of the many factors affecting cation availability.

16.6 Organic Matter Content

16.6.1 It is often stated that increased organic matter content will decrease plant uptake of cadmium by complexing it and thus rendering it unavailable (Brady 1984, WHO 1992). However, complexation with certain organic ligands causes the cadmium to remain in solution over a very wide range of pH values (Farrah et al. 1977). The role of organic matter is further complicated by the fact that the presence of cadmium inhibits the degradation of leaf litter and so decreases the amount of fulvic acid present; the organic component with which it principally binds. In general, cadmium binds strongly to organic matter components and relatively weakly to clay minerals, except in high pH soils when binding to clay is significantly higher (Coughtrey et al. 1983).

16.7 Cadmium in Fertilisers

16.7.1 Usage of phosphate fertilisers results in cadmium application to the soil surface. Cadmium content of fertiliser varies widely depending on the origin. Annual input resulting from fertilisers is estimated to be some 100 times less than the burden already present in the soil (Hutton 1982, WHO 1992). Despite this small size of input, long term continuous application has been shown to increase the soil burden (Andersson et al. 1981) although the increase is much less than when sewage sludge is added to the soil (OECD 1993).

16.7.2 On a national or regional basis however, the input to agricultural soils is significant and greater than that resulting from sludge application (Davis et al. 1980, WHO 1992). Cadmium added as a component of superphosphate fertiliser is water soluble (mainly sulphate and phosphate) and is thus very readily available to the plant. Most is retained within the top 10 centimetres of the soil and exists mainly as an exchangeable cation (Williams et al. 1973) and so, small changes in soil conditions, such as a minor decrease in pH, could result in significant amounts being released into the soil solution.

16.8 Cadmium in Sewage Sludge

16.8.1 Calculations estimate the amount of cadmium added to soils from this source to be 7.5mg/kg (DoE 1992). Cadmium added to agricultural soils as a result of sludge application accumulates in the top soil (OECD 1993) and is most available for crop uptake in the period immediately after the application and mixing of the sludge with the soil. Thus, the amount of cadmium available for uptake by plants is considerably more dependent on the amount in the last application than the cumulative total over time (Davies et al. 1980).

16.8.2 Whilst much of the cadmium in sludge is present in insoluble forms, such as hydroxides, carbonates or sulphides, some is adsorbed to organic matter. The rapid microbial decomposition of this organic matter that occurs after the addition of sludge to the soils, results in some of this cadmium becoming temporarily available in the soil solution. It becomes gradually less available as it is adsorbed onto soil constituents forming insoluble complexes. The degree to which this occurs depends on various soil factors but is not thought by (Davis et al. 1980) to involve the organic content of the sludge, although organic matter applied in the sludge increases the metal adsorbing capacity of the soil (Alloway 1990).

16.8.3 As a result of this gradual decrease in availability and retention in the zone of incorporation (0-15cm depth), it would appear from these data that there is little cause for concern as far as leaching through to the water table is concerned. However, other studies have found that cadmium may transfer from the surface soil (0-25cm depth) to lower levels (OECD 1993), that high levels of readily extractable cadmium persist some eight years after termination of sludge application (Berrow et al. 1979) and that almost 50% of the total applied is readily available to plants (Berrow et al. 1972).

In general, the literature concerning cadmium mobility in soils is extremely contradictory: 'cadmium tends to be more mobile in soils..than many other heavy metals'; (Alloway 1990) and 'cadmium is rather immobile in soil.. and ..accumulates in the top soil with no evidence of rapid downward movement..'(OECD 1993).

16.9 Mercury in Soils

16.9.1 The major input of mercury to soils results from atmospheric fall-out, with sewage sludge and fertilisers providing secondary sources as discussed previously for cadmium. A significant input of organic mercury used to result from its application as a seed dressing to reduce fungicidal infection although this use is now banned in the UK.

16.9.2 Typical levels in soils range between 0.06-0.36μg/g (Wiersma et al. 1986). Adsorption is the dominant process in the retention of mercury in soils. This is dependent on a number of factors; species of mercury, grain size distribution of the soil, nature and amount of inorganic and organic soil colloid, soil pH, chloride and sulphide ion concentration and redox potential (Stiennes 1990).

16.10 Organic Matter Content and pH; their effect on plant uptake and volatilisation

16.10.1 Mercury has a very high affinity for organic matter resulting in very small losses downward due to leaching (OECD 1993, Stiennes 1990) as organic matter is concentrated in the surface of the soil. However, lateral transport to water courses may occur during periods of run-off. At acid pH, the bonds in the organomercury compounds are so strong that transport of the carrier organic matter is virtually a prerequisite for mercury movement (Rundgren et al. 1992). As pH increases, the bond strength in these compounds decreases and adsorption to clay micelles becomes increasingly important (Stiennes, 1990), resulting in the formation of insoluble complexes; inorganic mercury exhibits the strongest affinity for clay amongst all the important toxic metals (Pequegnat 1988). Humic soils can therefore carry large amounts of mercury, the humic acids subsequently complexing on clay polymers with adsorption strength depending on pH (Jonasson 1970).

16.10.2 Under natural conditions, the release of elemental mercury vapour (Hg^0) from the soil is probably significant in the global mercury cycle (Stiennes 1990). Experimental evidence indicates that organic matter content tends to enhance the loss by volatilisation of inorganic salts added to the soil and that the reaction appears to be mediated by microorganisms (Rogers et al. 1979).

16.10.3 The ability to methylate mercury exists in a wide variety of microorganisms and so conditions which promote bacterial growth will, in general, lead to enhanced methylation of mercury (Jernelov 1973). Thus, increased organic matter content will provide a larger amount of substrate for the bacteria which will in turn, increase in population more rapidly and so produce more methyl- and, ultimately volatile dimethyl- mercury.

16.10.4 Whilst the strong bonds formed at acid pH decrease the amount of mercury available for plant uptake there is a complication as low pH favours the biotransformation of mercury into methyl mercury compounds (Kothny 1970) and thus increases plant uptake as this is the form most readily absorbed (Brady 1984). The mercury must be present in solution for reduction and subsequent loss by volatilisation (Stiennes 1990) and so binding to clay micelles and formation of sparingly soluble organic complexes will thus decrease the amount of mercury leaving the soil by this route.

16.10.5 Further conflicting evidence is that the presence of a high humus content in acid soil inhibited the vaporisation of mercury when it was present at 1µg/g whilst at higher mercury concentrations, losses were increased with higher humus contents (Wimmer 1974).

16.10.6 Coniferae litter accumulate gaseous mercury in preference to organically complexes mercury and so will reduce the amount escaping from the soil (Trost et al. 1970). Thus, while the presence of the conifers causes pH to tend towards acidic conditions and possibly increased availability, the litter will reduce the amounts of mercury vapour reaching the atmosphere while the coniferae in general have been found to have the highest uptake of mercury out of all plants studied (Warren et al. 1966).

16.11 Effects of Chloride and Sulphide Ions

16.11.1 In acidic conditions mercury exists as a chloride complex. Above pH 7, a hydroxide complex is the corresponding stable form. In the absence of chloride ions, sorption of mercury was found to decrease as pH increased, i.e. more mercury became available as acidity was reduced. Addition of chloride caused sorption to increase between pH4 and 6 and then decrease (Berrow 1992).

16.11.2 In reducing or neutral soils with a free sulphur or excess organic matter content, the mercury is very strongly bound, probably as insoluble sulphide or organic complexes and is thus unavailable to plants (Kothny 1973). Under these conditions, methyl mercury formation is also minimised (Pequegnat 1988) and so plant uptake is further reduced and losses by volatilisation are also decreased.

16.12 Mercury in fertilisers

16.12.1 Fertilisers, liming and manure can account for a substantial input of mercury into the soil (Andersson, 1979). The majority of commercial fertilisers have mercury contents below 50ng/g but higher values can occur. The mercury may derive partly from the phosphate rocks themselves and partly from the sulphuric acid used for their dissolution (Stiennes 1990). Lime tends to have concentrations below 20ng/g whilst mercury content of manure can be of the order of 100ng/g. Thus, while cadmium availability may be reduced by liming, an increase in soil mercury content may result.

16.13 Mercury in Sewage Sludge

16.13.1 The increase in soil mercury content caused by the addition of sewage sludge represents a significant increase with respect to background levels (Stiennes 1990). Calculations based on the 1991 DoE statistics (DoE 1992) estimate the amount of mercury in sewage sludge added to soils to be 3.7mg/kg (total sludge disposed of to farmland was 479,000 tonnes dry weight).

16.13.2 The majority of the literature reviewed for both metals appears to make broad generalisations which, when investigated further are often found to be inconsistent. In fact, the applicability of the literature concerning mercury is called into question by the following excerpt (from Dobson et al. 1989);

> '..the main problem with studies on the effects of mercury in terrestrial plants is their relevance to the natural situation. Mercury normally binds to soil particles, which may reduce its availability to plants. In most studies, mercury has been administered as a solution in hydroponic culture..'.

16.14 Conclusion

16.14.1 We conclude therefore, that even though there are significant amounts of cadmium and mercury contained in soils, there is an absence so far of conclusive data detailing their behaviour with respect to water especially in the longer term.

REFERENCES

See Section 17

17. BODYBURDENS

In this section we review the concept that in the absence of industrial mercury and cadmium discharges, the metal burden from domestic human sources may be significant. Mercury and cadmium are present in trace amounts in the air breathed and water and foodstuffs ingested by higher organisms including humans. Waste materials voided from humans typically reach the public sewerage and thence to the waste water treatment plant; therefore mercury and cadmium from human bodyburden sources may be a significant, intractable contribution to the overall metal mass balance.

As a result of continuous exposure to cadmium and mercury, organisms will accumulate these metals to varying degrees depending on the species of metal involved and the position of the organism in the food chain. The amounts absorbed by different organisms vary widely as does the retention time for the metals. The amounts present in the biomass constitute a temporary reservoir, the longevity of which is dependent upon retention time and the lifespan of the organisms under consideration. After death, various decay/disposal processes may result in the metals becoming available to the environment, e.g. burning of crop residues or cremation lead to atmospheric or terrestrial inputs.

17.1 Cadmium - Content in Foodstuffs

17.1.1 Meat, fish and fruit generally contain similar amounts of cadmium; 5-10μg/kg wet weight. Plant based foodstuffs are generally higher; 25μg/kg wet weight is considered representative (WHO 1992). Drinking water usually contains very low concentrations; 0.1-2.0μg/l although levels of 5-10μg/l have been reported (Swedish EPB 1985).

17.2 Air concentrations

17.2.1 Average air concentrations from various European countries are as follows:

- Rural: 1-5 ng/m^3
- Urban: 5-15 ng/m^3
- Industrial: 15-50 ng/m^3 (WHO 1987).

Levels in the UK rarely exceed 0.02-0.03 μg/m^3, even in industrial areas (DoE 1980).

17.3 Estimated intakes from all Environmental Pathways

Uncontaminated Areas

17.3.1 Assuming a daily inhalation rate for an adult of 15 m^3, and an average air concentration of 10 ng/m^3, this will result in a daily intake of 0.15 μg of which, about 25% (0.04μg) will be absorbed (Friberg et al. 1974).

17.3.2 Daily dietary intakes in Europe are estimated to be 10-25 μg per day, whilst intake from drinking water based on a consumption of 2 litres is thought to be less than 1μg (WHO 1992). At an absorption factor of 5%, the daily uptake of Cd from food and water would be 0.6-1.3 μg (WHO 1992). In general, dietary uptake is considerably more important than inhalation as a source of exposure when considering non-smoking members of the general population (WHO 1987).

17.3.3 Smoking 20 cigarettes daily can result in inhalation of 2-4 μg; the amount varies considerably depending on country of origin of the tobacco. Of this amount, 25-50% may be absorbed by the lungs resulting in an uptake of 1-2 μg (WHO 1992). Thus, heavy smokers can virtually double their daily uptake of cadmium.

Contaminated Areas

17.3.4 Airborne levels may reach 0.5 μg/m^3, resulting in a daily inhalation of 7.5 μg and absorption of about 2 μg (WHO 1992).

17.3.5 Intake from food and water varies considerably, depending on the reliance on locally grown food items. Intakes of 150-200 μg have been reported in areas where consumption of locally grown items was considerable.

17.3.6 Total daily uptake will depend on the nature and extent of the contamination, i.e. whether food, water, air or all three are contaminated but it is unlikely that it will exceed 20 μg (WHO 1992) under any circumstances.

17.3.7 In people not excessively exposed to cadmium, the range of accumulation up to the age of 50 has been estimated to be 10-80 mg whole bodyburden (Friberg et al. 1974)

17.4 Excretion

17.4.1 Studies have shown that urinary excretion of cadmium (measured in μg/l) increases with age (Kowal et al. 1979), this increase coinciding with the increased body burden and so smokers, who have a higher bodyburden than non-smokers, also excrete more. The mean urinary concentration in people not exposed to high levels varies from <0.5 to 2.0 μg/l (WHO 1992). This represents approximately 0.01% of the total body burden. There appears to be little available literature concerning the gastro-intestinal excretion of cadmium but it is believed to be very low (MAFF 1983). Almost one third of the total bodyburden accumulates in the kidneys of mammals and estimates of the biological half-life vary widely. Available experimental and epidemiological evidence indicates however that it is very long, of the order of 30 years (ECH 1992) although certain studies have found it to be much less than this.

17.4.2 As a result of the relatively low excretion of cadmium and its concentration within certain organs, consumption of offal will obviously lead to an increased dietary intake. The long half-life means that cremation of bodies will also result in cadmium being returned to the atmosphere.

17.5 Mercury - Content in Foodstuffs

17.5.1 Average levels in a variety of foodstuffs, excluding fish, have been estimated to lie within the range 0-100 µg/kg (wet weight) with the majority being about 20 µg/kg (WHO 1976; Somers 1971). Fish can accumulate mercury to significant levels; the normal concentrations in edible tissues of various fish species cover a considerable range from 50-1400 µg/kg fresh weight (WHO 1987). Mercury in fish appears to be predominantly methyl mercury whilst the species content of other foodstuffs appears to be variable. Drinking water content varies between 5-100 ng/l with a mean of about 25 ng/l (WHO 1987).

17.6 Air Concentrations

17.6.1 Estimates of ambient air concentrations vary widely between 1-1000 ng/m^3 (EPA 1984). Recent data estimates the UK concentration of particulate mercury to be 0.08-0.09 ng/m^3 at rural sites and 0.2-0.5 ng/m^3 at urban sites; concentration of mercury vapour was not measured (Lee et al. 1993). Air is the only human source of exposure to Hg^0. Recent figures estimate european rural concentrations of 2 ng/m^3 and urban concentrations of 10 ng/m^3 (WHO 1987).

17.7 Estimated Intakes from all Environmental Pathways

17.7.1 The daily amount absorbed into the bloodstream of adults as a result of respiratory exposure is estimated to be 32 ng in rural areas and 160 ng in urban areas, assuming the concentrations quoted above and that the majority (80%) of the inhaled elemental vapour is absorbed across the alveolar membranes and retained (WHO 1976; WHO 1987). Gastro-intestinal uptake varies considerably depending on the species of mercury concerned (WHO 1976; WHO 1987):

- f_1 metallic: 0.01%
- f_1 inorganic: 10-15%
- f_1 vapour: 80%
- f_1 organic: 80-90% where f_1 is the gastro-intestinal transfer factor.

17.7.2 The intake from drinking water is about 50 ng per day, only a small amount of which (5 ng) is absorbed. This is because the mercury in drinking water is mainly present as the Hg^{2+} salt.

17.7.3 Dietary intake from foodstuffs other than fish is difficult to estimate. Total levels are often close to the detection limit and the species of mercury involved are usually unknown. Intake of fish and fish products averaged over several weeks results in a daily retention of approximately 3000 ng. Daily intakes of methyl Hg, the predominant compound in fish, give a steady state balance in about 1 year when the body burden will be approx 100 times daily intake (WHO, 1976).

The total dietary intake measured in the USA over several years found a total average daily intake of 2000-7000 ng for adults, ≤ 1000 ng for toddlers and infants (estimated over the period 1973-82).

More recent data for the fiscal year 1981-82: 3000 ng for adults, 1000 ng for toddlers and <1000 ng for infants (EPA 1984).

17.8 Excretion

17.8.1 It is imperative to know the species of mercury under consideration, so that the relative amounts being absorbed and immediately excreted can be calculated. The low uptake of inorganic salts will lead to an immediate release to the environment whilst the high uptake of organics *in the* gut and metallic vapour in the lungs will delay release for a period of time dependent upon the biological half-life. Another source of exposure to mercury, in man at least, is caused by amalgam dental fillings which constantly release small amounts of the metal into the buccal cavity.

17.8.2 Urine and faeces are the principal routes of elimination of mercury from the body. The relative contribution of each depends upon the type of mercury compound and the time elapsed after exposure. Occupational exposure to 50 ng/m^3 for a period of at least six months will cause urine concentrations of about 150 µg/l (WHO 1976).

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