

# **Metal manufacturing, refining and finishing works**

*precious metal recovery works*



Industry Profiles, together with the Contaminated Land Research Report series, are financed under the Department of the Environment's contaminated land research programme.

The purpose of these publications is to provide regulators, developers and other interested parties with authoritative and researched advice on how best to identify, assess and tackle the problems associated with land contamination. The publications cannot address the specific circumstances of each site, since every site is unique. Anyone using the information in a publication must, therefore, make appropriate and specific assessments of any particular site or group of sites. Neither the Department or the contractor it employs can accept liabilities resulting from the use or interpretation of the contents of the publications.

The Department's Contaminated Land Research Report series deals with information needed to assess risks; procedures for categorising and assessing risks; and evaluation and selection of remedial measures.

General guidance on assessing contaminated land and developing remedial solutions which is complementary to the Department's publications is provided by the Construction Industry Research and Information Association (CIRIA).

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# DOE Industry Profile

## Metal manufacturing, refining and finishing works: precious metal recovery works

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*This Profile is based on work by Dames and Moore International and was prepared for publication by the Building Research Establishment.*

## Preface

DOE Industry Profiles provide developers, local authorities and anyone else interested in contaminated land, with information on the processes, materials and wastes associated with individual industries. They are not definitive studies but they introduce some of the technical considerations that need to be borne in mind at the start of an investigation for possible contamination.

Every site is unique. Investigation of a site should begin with documentary research to establish past uses. Information on the site's history helps to focus a more detailed investigation. This knowledge needs to be supplemented by information on the type of contamination that may be present and where on site it may be found. Profiles give information on the contamination which might be associated with specific industries, factors that affect the likely presence of contamination, the effect of mobility of contaminants and guidance on potential contaminants.

The date when industrial practices first commenced on a site and its location are important clues in establishing the types of operations that may have taken place, so each profile provides a summary of the history of the industry and its likely geographical spread within the United Kingdom.

Profiles should be read with the following reservations in mind:

- individual sites will not necessarily have all of the characteristics described in the profile of that industry;

- practices can vary between sites and change over time;

- as practices change, problems of possible contamination may also change;

- the profile may refer to practices which are no longer followed, and may omit current practices which avoid contamination.

The risks presented by contaminated sites depend on the nature of the contaminants, the targets to which they are a potential threat (such as humans or groundwater) and the routes or pathways by which they reach these targets. The current or proposed use of a site and its environmental setting are crucial in deciding whether treatment is necessary and if so, the methods to be used. Some sites may not need treatment.

The information in profiles may help in carrying out Control of Substances Hazardous to Health (COSHH) assessments for work on contaminated land - see Health and Safety Guidance Note HS(G) 66 *Protection of workers and the general public during the development of contaminated land*, Health and Safety Executive, 1991, and *A guide to safe working practices for contaminated sites*, Construction Industry Research and Information Association, 1995.

Note: the chemical names given to substances in this profile are often not the modern chemical nomenclature, but the names used historically for those substances.

# **Metal manufacturing, refining and finishing works: precious metal recovery works**

## **1. Background**

This profile deals with the recovery of precious metals from various sources, including sub-standard ingots, jewellery, photographic wastes, computers and printed circuit boards. The major precious metals recovered in the United Kingdom are gold, platinum, palladium and silver.

### **1.1 History**

Precious metals recovery in the United Kingdom dates back many centuries, particularly for the recovery of gold, silver and the platinum group metals (PGMs).

The modern history of the industry has been influenced by a number of events. Gold recovery capabilities expanded in the United Kingdom in the late 19th Century, as a result of the increased volume of gold entering the market due to the North American Gold Rush. The early black and white film processing industry produced large amounts of silver for recovery (modern film has a lower silver content). Development of catalytic petrochemical and chemical processes this century has resulted in a large increase in the amount of precious metals requiring recovery, particularly PGMs. The development of the electronics and computer industries since the 1960s has led to an increase in recycling of precious metals from these sources.

Early recovery processes used large quantities of chemicals and energy but during this century technological changes have reduced these demands.

### **1.2 Location**

Precious metals have traditionally been recovered near to the jewellery quarters of major cities, eg London and Birmingham. There was also recovery associated with the colouration and painting of pottery and other ceramics, eg Stoke-on-Trent. This geographical distribution has not altered greatly over time.

Modern sites, which often only deal with gold recovery, are normally located around larger conurbations or near large chemical complexes.

Census of production data show that in the late 1920s there were about 60 recovery establishments, falling to about 40 in the late 1930s, with numbers increasing after the Second World War. About half of the establishments employed less than 25 people.

It is understood from the industry that there are now about 100 works operating in the United Kingdom, the majority of which are small or medium sized facilities. There are three large refinery works in the United Kingdom, located in London and the South-East of England.

## **2. Activities**

Typically, the raw materials are treated either pyrometallurgically or chemically to regenerate the different precious metals. The actual recovery or refining processes involved are dependant on the quality of raw materials received and the presence of impurities.

The final products of recovery include metal bars, metallic matrices and compounds as well as precious metal products which may be returned to the supplier, transferred to an outside broker or sold directly to a third party.

### **2.1 Raw and process materials**

#### *2.1.1 Nature*

Raw materials can be liquids, sludges or solids, and include scrap jewellery, sub-standard ingots, industrial catalysts, discarded electronic circuitry, sludges and wastewaters, for example from photographic processing and silver plating. In general, precious metal recovery works receive a mixture of waste materials from a wide range of suppliers that may include petrochemical, pharmaceutical and chemical plants.

The substances used in the recovery processes can be in either solid, liquid or gaseous forms. They may include acids, fluxes, sand, cooling water, modifying chemicals, liquid chlorine, and a variety of organic and inorganic solvents. Some works use liquefied flammable gases as burner fuels for smelting, and nitrogen to provide an inert atmosphere when working with flammable materials.

#### *2.1.2 Method of delivery*

Raw and process materials are delivered to site either in bulk quantities (eg large volumes of metal waste and scrap) or in smaller quantities (eg gold scrap or sweepings). Fuel oil or gas for burning, smelting and similar operations are delivered by bulk road tanker or by direct pipeline. Acids, alkalis and solvents are typically delivered by bulk road tanker. Chemicals which are used in smaller quantities are delivered in drums, kegs and intermediate bulk containers. Coke used for pyrometallurgical processes and fluxes are received in bulk, primarily by road transport, and usually stored in uncovered areas, often directly on unprotected soil. Large recovery plants may also incorporate research and laboratory facilities and therefore may receive and store a wide variety of chemicals, typically in small quantities.

#### *2.1.3 Transfer of materials*

Raw materials are transferred within the recovery plant using a variety of methods depending on their physical state and quantity. Solids (which include resins, computers, gold jewellery and ingots) are transferred using a combination of mechanical means, eg fork-lift trucks, conveyors, cranes and manual systems. Pumped systems are typically used for molten metal, sludges/suspensions, acids and alkalis, and solvents that are in a liquid or semi-liquid state. Kegs, bags and bottles of chemicals are often handled manually by site personnel.

Operations at the many works involved with the casting of ingots may entail the use of degreasing agents, eg chlorinated hydrocarbons. These are generally stored in

bulk storage tanks or drums and either pumped from the tanks or transferred in drums to the place of use.

## **2.2 Recovery processes and products**

Generally, the types of processes used in precious metal recovery depend on the quality of the received materials and the interests of the company. Depending on their quality and state prior to refining, the raw materials may be first processed to produce a metal concentrate by chemical treatment, burning or drying, and melting.

The metals most commonly recovered by the above processes are silver, gold and PGMs, for sale or for conversion into special weight bars of high purity. They are usually delivered from the works as ingots. Alternatively, they can be returned to the raw material supplier as precious metal compounds, catalysts or fabricated products.

Metals such as iron, tantalum, iridium, zinc, copper and aluminium, sometimes present as impurities in the raw materials brought onto a recovery site, may also be processed.

Most recovery works incorporate casting operations and possibly surface finishing operations to suit customer requirements.

### *2.2.1 Chemical and melting processes*

One chemical treatment is the precipitation of metals from solution by substitution using a more active metal such as iron, zinc, copper or aluminium at optimal pHs. Typical compounds used in silver precipitation processes include sodium sulphide, and acids and alkalis for pH control. Another treatment involves ion exchange resins which are widely used for the removal of precious metals (particularly silver) from wastewaters. The resins can be regenerated using a variety of chemicals, including acids, brine and ammonium chloride or thiosulphate, producing solutions containing the precious metals, which are generally sent for electrolytic refining. However, for the highest value metals such as gold, the spent resins may be burnt in a crucible type unit, leaving a residue of molten gold metal and other metal impurities. The use of organic solvents to extract metals from waste solutions is another chemical treatment.

Metal scrap, such as low grade bullion and jewellery, is usually melted and then subjected to pyrometallurgical processing. In smelting operations using a blast furnace, the scrap is mixed and processed along with coke and fluxes (eg litharge and borax). The resulting molten metal concentrate is then typically subjected to the cupellation process: oxygen is blown across the metal to volatilise some of the minor metals present and to remove any iron and residual copper and lead oxides as dross. The remaining molten metals can then be cast as electrodes and subjected to electrolytic processing to produce a refined product. Alternatively they can be cast into pellets and treated with nitric acid to remove base metals. Sulphuric acid is often used if the lead content of the pellets is low.

Very low grade scrap may be melted, cast into anodes and electrolysed in a sulphate salt solution. The gold, which remains in the electrolytic vessel as a mud, is recovered by converting it to gold chloride (possibly by bubbling chlorine gas

through the bath) and then precipitating the gold using ferrous sulphate and pH control. If further purification is required, the gold precipitate can be removed, dried, melted and cast into anodes for electrolytic refining.

### *2.2.2 Electrolytic refining*

Refining of gold concentrates can be achieved using the Wohlwill process in which pure gold is recovered from a chloride solution using alternative use of DC and AC currents and collecting the gold on the cathode. The gold is flaked off the cathodes which are usually made from stainless steel.

The solution remaining after electrolysis may contain other PGMs which can be separated using a variety of techniques. For example, platinum is separated from the solution by dibutyl carbinol solvent extraction, followed by a series of treatments using ammonium chloride, sodium chloride, aqua regia and bromate solutions. A combination of processes involving formic acid, ammonia and hydrochloric acid can be used to separate out palladium after platinum removal.

## **2.3 Ancillary activities**

Larger works may include on-site steam and power generation facilities for site services, and raw-water purification and wastewater treatment plants, all of which may involve the storage and use of a wide variety of fuels and chemicals including acids and alkalis.

## **2.4 Wastes**

Owing to the high value of precious metals, gold is first recovered from the wastes and the resulting sludges/liquids are transported to another works or company for further treatment, ie the recovery of PGMs.

Pyrometallurgical operations produce an acidic solution containing metal nitrates, slag and dross which may be manually or automatically removed. This is usually transferred in small containers to an open area, generally constructed from concrete, and cooled using water sprays. Where practicable and economical, dross and slag containing iron, lead and other lower value metals are sold to third parties for further metal recovery.

Waste materials are generally stored in drums or vessels in properly designed compounds. In the past, wastes may have been stored in open areas in direct contact with the soil.

Generally, waste materials are collected and stored until sufficient quantities are amassed for cost-effective disposal, normally to landfill by an outside contractor. These wastes may include plastic and metal drums, general industrial site waste and refractory materials, as well as residues from pollution control processes.

On larger sites there may be wastewater treatment plants which generate sludge wastes for off-site disposal.

In the past, some waste materials may also have been disposed of in landfill areas on site or deposited directly on to the soil surface.

### **3. Contamination**

The contaminants on a site will largely depend on the history of the site and on the range of materials produced there. Potential contaminants are listed in the Annex and the probable locations on site of the main groups of contaminants are shown in Table 1. It is most unlikely that any one site will contain all of the contaminants listed. It is recommended that an appropriate site investigation be carried out to determine the exact nature of the contamination associated with individual sites.

#### **3.1 Factors affecting contamination**

The major potential for soil contamination from process related operations comes from the storage of charcoal/anthracite/coke, from slag/dross removed from smelting operations and from the transfer, storage and process areas where aqua regia and other acids and organic solvents have been used.

Localised contamination may result from bulk storage facilities; this may include fuel oil, degreasing/cleaning solvents and acids and alkalis for wastewater treatment. Historically, storage areas for fuel oil and solvents and their loading and off-loading areas may not have been contained. The environmental security of the storage and handling systems would largely depend on the site's materials and waste management practices during the lifetime of the facility.

Ancillary chemicals that may be present on site include wastewater treatment chemicals, fuel oils, maintenance oils and greases. Often, large sites have underground storage tanks for these materials. Leakage from both underground and above-ground storage may have caused ground contamination.

Any metal contamination is probably localised in areas where spent refractory materials, slags and drosses are handled, and in storage areas for waste sludges and solutions containing metals. In the past, fall-out of metals from process exhaust emissions may have produced surface contamination around a works but such contamination is likely to be insignificant. Modern plant typically contains pollution control and abatement systems to minimise air pollution, and to contain safely wastes which are stored on site prior to disposal.

Generally there is an extensive requirement for insulation of pipes and vessels. In the past the materials used for lagging may have contained asbestos. Buildings may also contain asbestos-cement sheeting for roofing and cladding.

After close down, decommissioning and demolition, asbestos and other contamination may have occurred through indiscriminate spillage of residual stock, or from moving wastes about the site.

Many works have their own electrical sub-stations, particularly if electric furnaces are used. In the past, sub-stations may have contained polychlorinated biphenyls (PCBs) in transformers and/or capacitors.

## 3.2 Migration and persistence of contaminants

### 3.2.1 Metals

Although there is a high potential for heavy metal contamination to occur, the metals may be in an immobile form, particularly if associated with slag or dross which contain the most immobile forms of metals (eg copper and lead oxides). Metals released from the processes have varying degrees of solubility, depending upon the nature of the associated anion; in many cases the oxides and sulphides are of low solubility and concentrations are likely to decrease with depth. However, metal and other inorganic sulphates could have significant mobility in soil.

The movement of metals through the soil is significantly retarded by the presence of clay minerals and organic matter. The solubility of some metals (eg copper, zinc and lead) may increase under acidic conditions. In other cases the relationship is more complex. For example, trivalent chromium is more soluble under acidic conditions, whereas the solubility of hexavalent chromium is increased under both acidic and alkaline conditions and arsenic may become more soluble at higher pHs.

### 3.2.2 Organic compounds

The organic solvents likely to be encountered (arising, for example, as cleaning and degreasing agents) are volatile and have moderate to high vapour pressures. After an extensive spill, they may migrate to the water table. The liquids vaporise readily, resulting in high concentrations in the soil pore space above the saturated zone. Close to the soil surface, some are lost directly to the atmosphere by evaporation. Although the solubility of some of these solvents is relatively low, their dissolved concentrations may be greater than water quality standards permit.

In most cases, organic compounds are less dense than water and therefore float on the surface of the water table. However, chlorinated solvents are denser than water and tend to migrate to the bottom of any water body. Their migration may not be consistent with the general groundwater flow. They are persistent chemicals and at low concentrations can exceed water quality standards.

As with metals, the transport and fate of organic compounds within the sub-surface environment is dependent upon physical, chemical and biological factors. The higher the natural organic matter and clay content of the soil, the greater the adsorption of the organic compounds and the lesser the contaminant migration. Thus, the greatest degree of migration occurs in coarse-grained sands and gravels with little natural organic matter. The less-soluble compounds, which become adsorbed on to clay or organic matter, may provide on-going sources of water pollution long after the source of contamination has been removed, by continuing to desorb into the soil water. The risk from organic chemicals to current and potential water supplies may therefore be considerable. Lateral movement through the soil, either in the dissolved or free phase, may also affect surface water.

### 3.2.3 Other factors

Asbestos is neither soluble nor biodegradable and persists in the soil. Wind dispersion of contaminated soil may be a further transport mechanism where there is gross surface contamination by some of the less-mobile contaminants, particularly metals and asbestos.

PCBs and some of the halogenated organics are fat-soluble and have a propensity to accumulate in food chains.

A fire in storage or other areas of a works could result in contamination through the spillage of liquids or other potentially fugitive material or, for example, through dispersion from the run-off of fire-fighting water.

## **4. Sources of further information**

### **4.1 Organisations**

For information concerning the precious metals recovery industry in the United Kingdom, the following organisations should be consulted:

The Institute of Materials  
1 Carlton House Terrace  
London  
SW1Y 5DB

The Institute of Metal Finishing  
48 Holloway Head  
Birmingham  
B1 1NQ

The Institution of Mining and Metallurgy  
44 Portland Place  
London  
W1N 4BR

### **4.2 Sources of further information concerning the activities described in this profile**

**Alcock C B.** *Principles of pyrometallurgy.* Academic Press, 1976.

**Alexander W and Street A.** *Metals in the service of man.* London, Penguin, 1989.

**Austin G T.** *Shreve's chemical process industries.* 5th Edition. London, McGraw-Hill, 1984.

**Dragun J.** *The soil chemistry of hazardous materials.* Silver Spring MD (USA), Hazardous Materials Control Research Institute, 1988.

**Eckroth D, Graber E, Kingsberg A and Siegel P M.** *Kirk-Othmer concise encyclopaedia of chemical technology.* Chichester, John Wiley and Sons, 1985.

**Higgin R A.** *Properties of engineering materials.* Sevenoaks, Hodder and Stoughton, 1980.

**Kellet B.** *Gold.* Graham and Trotman, 1982.

**Perry R H and Chilton C H.** *Chemical engineers handbook*. 5th Edition. London, McGraw-Hill, 1973.

**Robb C.** *Metals databook*. London, Institute of Metals, 1987.

**Ryan W (Ed).** *Non-ferrous extractive metallurgy in the United Kingdom*. London, Institution of Mining and Metallurgy, 1968.

Case study including information relevant to this Industry Profile:

**Paul V.** *Bibliography of case studies on contaminated land: investigation, remediation and redevelopment*. Garston, Building Research Establishment, 1995.

Estimates of the size and geographical distribution of the precious metals recovery industry can be obtained from the following Central Government statistics, held principally by the Guildhall Library, Aldermanbury, London and the City Business Library, 1 Brewers Hall Garden, London:

*Census of production reports*. Board of Trade, HMSO (from 1924 to 1969).

*Business Monitor Series: Annual census of production reports*. Central Statistical Office, HMSO (from 1970 to date).

Information on researching the history of sites may be found in:

**Department of the Environment.** *Documentary research on industrial sites*. DOE, 1994.

### 4.3 Related DOE Industry Profile

Metal manufacturing, refining and finishing works: non-ferrous metal works (excluding lead works)

### 4.4 Health, safety and environmental risks

The Control of Substances Hazardous to Health (COSHH) Regulations 1994 and the Management of Health and Safety at Work Regulations 1992 are available from HMSO. Information on relevant health and safety legislation and approved codes of practice published by HSE publications are available from Health and Safety Executive Books, PO Box 1999, Sudbury, Suffolk, CO10 6FS (telephone 01787 881165), as well as HMSO and other retailers.

Information on the health, safety and environmental hazards associated with individual contaminants mentioned in this profile may be obtained from the following sources:

**Howard P H.** *Handbook of environmental fate and exposure data for organic chemicals*. Vols I and II. USA, Lewis Publishers, 1990.

**Sax N and Lewis R.** *Hazardous chemicals desk reference*. New York, Van Nostrand Reinhold Company, 1987.

**Verschuere** K. *Handbook of environmental data on organic chemicals*. 2nd Edition. New York, Van Nostrand Reinhold Company, 1983.

#### **4.5 Waste disposal and remediation options**

Useful information may be obtained from the Department of the Environment series of Waste Management Papers, which contain details of the nature of industrial waste arisings, their treatment and disposal. A current list of titles in this series is available from HMSO Publications Centre, PO Box 276, London, SW8 5DT.

Publications containing information on the treatment options available for the remediation of contaminated land sites, prepared with the support of the Department of the Environment's Research Programme, can be obtained from National Environmental Technology Centre Library, F6, Culham, Abingdon, Oxfordshire, OX14 3DB.

A full list of current titles of Government publications on all aspects of contaminated land can be obtained from CLL Division, Room A323, Department of the Environment, Romney House, 43 Marsham Street, London, SW1P 3PY.

Advice on the assessment and remediation of contaminated land is contained in guidance published by the Construction Industry Research and Information Association (CIRIA), 6 Storey's Gate, Westminster, London, SW1P 3AU.

## **Annex Potential contaminants**

The chemical compounds and other materials listed below generally reflect those associated with the industry and which have the potential to contaminate the ground. The list is not exhaustive; neither does it imply that all these chemicals might be present nor that they have caused contamination.

### **Principal process chemicals**

Solvents	dibutyl carbinol chlorinated hydrocarbons, eg carbon tetrachloride, dichloromethane
Acids	hydrochloric nitric sulphuric formic bromate solution
Alkalis	ammonium salts, eg ammonium chloride, ammonium thiosulphate
Modifying chemicals	sodium borohydride
Fluxes	sodium borate (borax) lead oxide (litharge)
Carbon	charcoal coke
Other chemicals	ammonia chlorine (liquid) sodium sulphide sodium chloride sodium sulphate ferrous sulphate ion exchange resins

### **Wastes/products**

Metals, metalloids and their compounds	arsenic cadmium chromium mercury gold silver platinum palladium lead iron zinc aluminium
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copper  
metal nitrates

Fuels

oils  
coal

Oils

lubricating oils and greases

Polychlorinated biphenyls  
(PCBs)

Refractory materials

Asbestos





## DOE Industry Profiles

Airports

Animal and animal products processing works

Asbestos manufacturing works

Ceramics, cement and asphalt manufacturing works

Chemical works: coatings (paints and printing inks) manufacturing works

Chemical works: cosmetics and toiletries manufacturing works

Chemical works: disinfectants manufacturing works

Chemical works: explosives, propellants and pyrotechnics manufacturing works

Chemical works: fertiliser manufacturing works

Chemical works: fine chemicals manufacturing works

Chemical works: inorganic chemicals manufacturing works

Chemical works: linoleum, vinyl and bitumen-based floor covering manufacturing works

Chemical works: mastics, sealants, adhesives and roofing felt manufacturing works

Chemical works: organic chemicals manufacturing works

Chemical works: pesticides manufacturing works

Chemical works: pharmaceuticals manufacturing works

Chemical works: rubber processing works (including works manufacturing tyres or other rubber products)

Chemical works: soap and detergent manufacturing works

Dockyards and dockland

Engineering works: aircraft manufacturing works

Engineering works: electrical and electronic equipment manufacturing works (including works manufacturing equipment containing PCBs)

Engineering works: mechanical engineering and ordnance works

Engineering works: railway engineering works

Engineering works: shipbuilding, repair and shipbreaking (including naval shipyards)

Engineering works: vehicle manufacturing works

Gas works, coke works and other coal carbonisation plants

Metal manufacturing, refining and finishing works: electroplating and other metal finishing works

Metal manufacturing, refining and finishing works: iron and steelworks

Metal manufacturing, refining and finishing works: lead works

Metal manufacturing, refining and finishing works: non-ferrous metal works (excluding lead works)

Metal manufacturing, refining and finishing works: precious metal recovery works

Oil refineries and bulk storage of crude oil and petroleum products

Power stations (excluding nuclear power stations)

Pulp and paper manufacturing works

Railway land

Road vehicle fuelling, service and repair: garages and filling stations

Road vehicle fuelling, service and repair: transport and haulage centres

Sewage works and sewage farms

Textile works and dye works

Timber products manufacturing works

Timber treatment works

Waste recycling, treatment and disposal sites: drum and tank cleaning and recycling plants

Waste recycling, treatment and disposal sites: hazardous waste treatment plants

Waste recycling, treatment and disposal sites: landfills and other waste treatment or waste disposal sites

Waste recycling, treatment and disposal sites: metal recycling sites

Waste recycling, treatment and disposal sites: solvent recovery works

Profile of miscellaneous industries incorporating:

Charcoal works

Dry-cleaners

Fibreglass and fibreglass resins manufacturing works

Glass manufacturing works

Photographic processing industry

Printing and bookbinding works

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