

***"Materials-Cycle Optimisation in the  
Production of Major Finished Materials"***  
**CHAPTER 3: COPPER, COBALT,  
SILVER & ARSENIC**

by

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This chapter is part of a report made for the EC DGXII on a project entitled **"Materials-Cycle Optimisation in the Production of Major Finished Materials"**. This project aims at facilitating the identification of longer-term R&D needs for materials-cycle optimisation, especially by using wastes, co-products, or by-products from one process as inputs to other processes. Book publication is envisaged. Following is the list of chapters:

- Chapter 1: Summary and Overview (*Insead ref N°: 95/05/EPS*)
- Chapter 2: Alumina, Aluminium and Gallium (*Insead ref N°: 95/06/EPS*)
- Chapter 3: Copper, Cobalt, Silver & Arsenic (*Insead ref N°: 95/07/EPS*)
- Chapter 4: Chromium Sources, Uses and Losses (*Insead ref N°: 95/08/EPS*)
- Chapter 5: Zinc and Cadmium (*Insead ref N°: 95/09/EPS*)
- Chapter 6: Sulfur and Sulfuric Acid (*Insead ref N°: 95/10/EPS*)
- Chapter 7: Phosphorus, Fluorine and Gypsum (*Insead ref N°: 95/11/EPS*)
- Chapter 8: Nitrogen-based Chemicals (*Insead ref N°: 95/12/EPS*)
- Chapter 9: The Chlor-Alkali Sector (*Insead ref: N°: 95/13/EPS*)
- Chapter 10: Electronic Grade Silicon (EGS) for Semiconductors (*Insead ref N°: 95/14/EPS*)
- Chapter 11: Packaging Wastes (*Insead ref N°: 95/15/EPS*)
- Chapter 12: Scrap Tires (*Insead ref N°: 95/16/EPS*)
- Chapter 13: Coal Ash: Sources and Possible Uses (*Insead ref N° 95/17/EPS*)

All chapters are individually available as INSEAD Working Papers.

## CHAPTER 3. COPPER, COBALT, SILVER & ARSENIC<sup>1</sup>

### 3.1. Summary

Copper is man's oldest metal (because it was found in workable nuggets) and remains one of the most important industrial metals because of its remarkable malleability, ductility, electrical and thermal conductivity and resistance to corrosion. Its red-orange color is also very attractive. For all of these reasons copper will continue to be used in many applications, especially tubing, pipe and electrical wire, notwithstanding strong competition from aluminum in some of them and glass fibers for others. Cobalt is also a very important industrial metal, particularly as a binder for ultra-hard carbides and an alloying agent for high temperature resistant superalloys (used in jet engines, for instance) and permanent magnets. Cobalt is so valuable for these properties that it is commonly regarded as a "critical" metal for modern aerospace technology.

The by-products of copper are zinc, lead, molybdenum, cobalt, arsenic, selenium, tellurium, and silver, as well as sulfur. These metals are often (but not always) found in the same ores, usually as sulfides. However, zinc, lead and molybdenum are primarily found in distinct ore bodies in which copper is a minor constituent, and which are mined for their own sake. (See *Chapter 5, Zinc*). This is partly, but less true of silver. Sulfur is a major by-product, but never a primary product. (See *Chapter 6, Sulfur*). Non-ferrous metal mining and smelting has long been a major sulfur dioxide polluter; it is an increasingly important source of sulfur for industry today. According to one source, 1.3 tonnes of sulfur dioxide are generated at the smelter for each tonne of pure primary copper. In the industrialized countries, most sulfur is captured, but elsewhere much of this sulfur is still emitted to the atmosphere as SO<sub>2</sub> rather than being recovered for useful purposes.

Moreover, copper ores are low in grade and most copper is mined from large open pit mines requiring large amounts of materials processing (in the U.S. 165 tonnes of inert material per tonne of Cu, exclusive of overburden), at high energy cost, to extract the virgin metal. Copper mining involves more materials displacement than any mining activity except coal mining and uranium mining, with all that this implies for physical damage to the environment.

Arsenic is a by-product of copper ore mostly used for its extraordinary bio-toxicity (e.g. in herbicides and wood preservatives). The distribution of arsenic in the environment is widespread and worrisome. It moves relatively easily from one environmental medium to another, e.g. from soil to air to water. Arsenical herbicides and pesticides, used in the past, can be taken up by plants, or metabolized by anaerobic bacteria to form methyl arsines which are extremely volatile. Airborne arsenic is a probable cause of cancer. Arsenic has an important potential electronic use (the semiconductor gallium arsenide), which could conceivably "soak up" some of the excess potential supply,<sup>2</sup> assuming gallium were also sufficiently available. (This appears to be the case: See *Chapter 2, Aluminum*).

Silver is used mainly for coinage, jewelry and decorative plating. However, it is still used extensively in photography, although this use is declining due to technological progress in photochemistry and increasing competition by electronic imaging technologies. It is important that silver be recovered to the maximum feasible extent, however, if only to conserve it for



Unfortunately, copper is relatively scarce in the earth's crust (58 ppm) and it is only found in rather low grade ores today, though a great many different minerals contain copper. It is now mined predominantly from relatively low grade porphyry (sulfide) ores from large open pit mines. Open pit mines account for 55% of the world output (83% in the U.S.).

U.S. ores now being mined average around 0.5% -0.6% Cu, although Chilean ores are about twice as rich and some Zambian/Zairian ores can be up to 5% Cu, though the average is around 1.2%. The main consequence of this fact is that large amounts of inert material must be processed to obtain a small amount of copper, resulting in large energy consumption and large quantities of mine waste. In the U.S. over 500 metric tons of inert material must be moved and over 165 metric tons of ore must be processed to produce a metric ton of virgin copper. A generalized flow-chart for copper is shown in *Figure 3.1.* above.

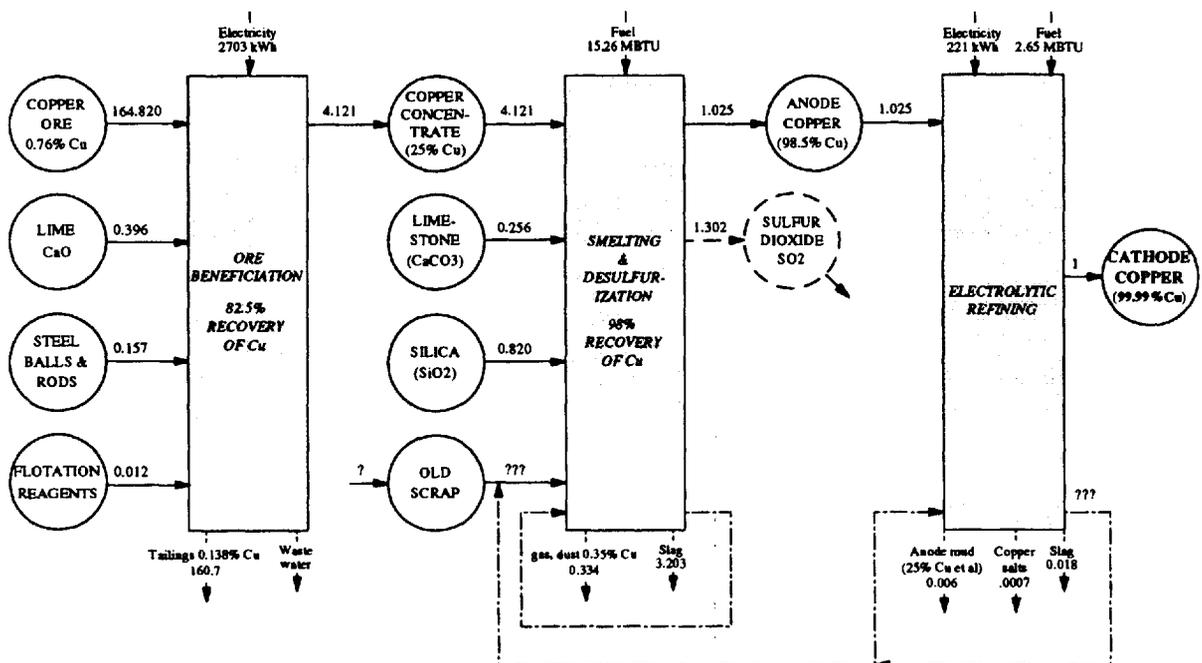


Figure 3.2. The "standard process" for copper

World mine production in 1989 was 8.89 MMT (Cu content); 1993 production was about the same, 9.3 MMT. Copper is mined in many countries, but the two principal producers in 1993 were Chile (2.02 MMT) and the U.S. (1.77 MMT). These were followed by Canada (750 KMT), the former USSR (800 KMT), Zaire (90 KMT, down sharply from 475 KMT in 1989), Zambia (420 KMT) and Poland (390 KMT). Other European sources are minor, as shown in *Table 3.1.* Output from older Scandinavian mines is declining; newly opened Portuguese mines are increasing output, however.

The "standard" process starts with ore from an open pit or underground mine. It is processed by crushing and grinding, concentrated by froth flotation, and the concentrate (30% Cu) is then reduced in a primary smelter to a copper sulfide-iron sulfide "matte" (up to 60% copper). The latter then passes to a "converter" in which the sulfur is removed (by oxidation to SO<sub>2</sub>)

which is later recovered as sulfuric acid. The convertor stage increasingly uses oxygen enrichment — a technology borrowed from the steel industry — and the iron is removed as convertor slag, yielding "blister copper". The latter is further "fire refined" in a furnace to produce anodes for the final electrolytic refining stage. A simplified process-product flow-chart for the standard process is shown in *Figure 3.2*. However, the figure is a composite that does not reflect the full range of technologies and changes now under way. The most active area of technological change is in the smelter technology, which is switching from reverberatory batch furnaces to flash furnaces and continuous smelters.

**Table 3.1. European copper mine, smelter, & refinery output 1991, kMT**

	Mine	Smelter		Refinery	
		Primary	Secondary	Primary	Secondary
<b>World Total</b>	<b>8819.5</b>	<b>8007.8</b>	<b>1044.0</b>	<b>8410.4</b>	<b>1495.3</b>
<b>Western Europe</b>	<b>300.1</b>	<b>490.9</b>	<b>263</b>	<b>815.1</b>	<b>615.4</b>
Austria				8.4	44.4
Belgium		0.2	100	185	102
Finland	11.7	90.1	12	56.5	8
France	0.3		9	16	30
Germany	9	191.2	82	306.5	216
Italy					82.5
Norway	17.4	38.4		38.5	
Portugal	165	1	2	6	
Spain	16	115	34	115	50
Sweden	80.5	84	24	66.1	30.5
United Kingdom	0.2			17.1	53
<b>Eastern Europe</b>	<b>586.6</b>	<b>517.5</b>	<b>67.6</b>	<b>522.5</b>	<b>68.7</b>
Albania	6.1	6		8	
Bulgaria	30	29	1	14	10
Czechoslovakia	2.5	2.5	15.5	2.5	15.5
Hungary			0.1		
Poland	390	360	20	378	19
Romania	20	25	1	20	2
Yugoslavia	138	95	30	100	22.2
Turkey	38.4	19.7	2	85	
USSR	550	700	120	750	120
USA	1631	1123	364.3	1577.4	417.8
Chile	1814.3	1296.1		1237.8	
<i>Source: [USBuMines 1991]</i>	<i>Table 30</i>	<i>Table 32</i>		<i>Table 31</i>	

The most important innovation (since 1968) is known as solvent extraction-electro-winning, or SX-EW technology. Certain ores (so-called "acid-soluble oxide" ores and chalcocite (CuS<sub>2</sub>))

ores) are leached with dilute sulfuric acid — a by-product of conventional smelters — in heaps, pads or even *in situ*. The next step is solvent extraction, using organic solvents. The concentrated copper sulfate then goes directly to an electrolytic cell to produce "cathode copper", thus by-passing both the smelting and refining steps. The SX-EW process has been under development for a long time, with gradually increasing yields and improvements in product quality, but by 1977 EW cathode copper was pure enough to go directly to wire-rod plants. U.S. output from this process was only 32.7 KMT in 1971, but reached 441 KMT in 1991 (27% of U.S. mine production) and is expected to peak at 690 KMT by 1998. World SX-EW capacity was 1.1 MMT in 1991 and will nearly double by the year 2000.

Curiously enough, while the new hydro-metallurgical process is economically favorable (and permits exploitation of low grade ores, including waste dumps from former mines) it is not an improvement over the standard pyro-metallurgical process in terms of energy consumption. This is due to the large amount of energy required to circulate the leachate. However, the energy used in electro-winning *per se* is only 20% of the total energy consumption from mine to refinery, so that energy may be used (or saved) at a number of different points, depending on the ore body. The energy consumed to produce a metric ton of refined copper ranges from 100 GJ (95 MMBTU) for high grade ore (1% Cu) to 200 GJ (190 MMBTU) for the lowest grade ore currently mined (0.3%) [Forrest & Szekely 1991].

Copper is normally concentrated at the mine and smelted to "blister" copper nearby, though a few smelters (mainly in Western Europe) use imported ores and concentrates. See *Table 3.1*. The biggest primary smelters in Western Europe are in Hamburg and Luenen, Germany (240 and 105 KMT capacity, respectively); Huelva, Asua-Bilbao and Barcelona, Spain (85, 30 and 24 KMT capacity, respectively); Ronnskar, Sweden (105 KMT capacity), Harjavalta, Finland (75 KMT capacity); and Kristiansand and Sulitjelma, Norway (30 and 9 KMT capacity, respectively). See *Table 3.1*. Portuguese ore is smelted and refined in Germany or (possibly) Spain. Smelters in Germany, Sweden and Finland all use at least some imported concentrates. Sweden exports concentrates to Finland and Germany; it imports concentrates from Chile, Greece (probably re-exported) and the U.S.

Sweden imports blister copper from various countries for refining. Some blister copper from Sweden is, in turn, exported and refined in the U.K., Netherlands and Finland. The Finnish smelter now obtains about 20% of its concentrates from Chile. The German smelters obtain their concentrates primarily from Portugal, Papua New Guinea and Chile. Similarly, the Belgian copper refineries import blister copper from Zaire, Zambia and the (former) USSR.

### 3.3. Copper Uses and Recycling

End uses of copper are mostly (97%) as metal. Pure refined copper is generally used for wire and wire products and copper tube, while copper alloys — especially brass (an alloy of copper and zinc) — are or were used for a variety of other products, such as architectural hardware, clocks and watches, bearings, coins, batteries, bronze castings, screws, ammunition, automobile radiators, air-conditioning, heat exchangers, and so on. Wire mill products accounted for about 51% of copper consumption in 1936 (the earliest available statistics) and only 43.5% in 1940, but since World War II this has risen steadily to 70% in 1980 and

probably over 80% today. By contrast, the relative importance of copper sheet, castings, and brass products has decreased sharply. Copper wire and pipe, and brass hardware are recovered and recycled to a significant degree. But a good deal of metallic copper is lost in solid wastes, especially discarded electrical appliances and consumer electronic devices.

In recent decades, industrial uses of copper chemicals, including catalysts (especially in aniline dye manufacturing), fungicides (mostly in vineyards) and wood preservatives, have been small and growing slowly. The case of wood preservatives — which also utilize arsenic — is discussed under (*Chapter 4, Chromium*) and need not be repeated here. Chemical uses amount to less than 3% of total copper consumption.

Secondary copper refined from old scrap accounts for only about 25% of current consumption in the U.S. [USBuMines 1991]. Most copper sulfate used to manufacture copper chemicals, especially for agriculture, is derived from scrap copper. If "new scrap" is included, the figure is significantly higher, of course. According to industry statistics [METALSTAT 1993], consumption of refined copper in the EEC in 1992 was 2.956 MMT, copper refined from scrap was 627 KMT (21.2 %) while total secondary copper scrap recovery was 787.5 KMT (26.5 %). The recovery rate for copper has been rising steadily, but it is still surprisingly low. We do not have reliable figures for individual countries in Europe, although West Germany reported 42% recycling in 1982 [BDI 1984].

The main reason the recycling rate is low is that much of the copper is used in long-lived products, such as appliances, vehicles and structures. Thus much of it is tied up for many years in "inventory". However, the fundamental problem is that disassembly of demolition waste and consumer products to recover electrical wiring buried inside is seldom worthwhile on economic grounds.

Yet there are strong arguments for encouraging more recycling of copper and its alloys (e.g. brass) to the maximum feasible degree, which should certainly be considerably higher than 25% or even 40%. This would reduce the need for mining and smelting of virgin copper, thus cutting down on most of the above sources of emissions, as well as reducing arsenic production at the source. The energy savings are compelling: the energy required to recover copper from scrap varies from 14 to 40 GJ/tonne, depending on the quality of the scrap, as compared to 100-200 GJ/tonne for virgin copper [Forrest & Szekely 1991].

Almost certainly the solution is not technological. That is to say, there is no imaginable machine or chemical process for extracting copper wires efficiently from a crushed automobile body, a washing machine, a TV set, or an electric clock, as now manufactured. Manufacturers, currently, take no responsibility for the ultimate disposal of their products, and they do not design their products for easy recyclability. Yet, in the case of copper, it seems likely that much could be done at the design stage of the manufacturing to facilitate easy removal of copper wiring and copper-bearing components (such as the windings of transformers and motors).

Even when products are designed to make it possible, disassembly will still be relatively labor intensive compared to original manufacturing. To make it happen — as opposed to making it *possible* — it will be necessary to accomplish either (or both) of the following: (1) to sharply increase the value (i.e. price) of copper *vis a vis* labor and (2) to encourage the export

of used consumer appliances to low wage countries where valuable materials can be separated and recovered for use at reasonable cost.

How either of these conditions is to be met is beyond the scope of the present study. However, it may be worth noting that a resource-based taxation system now being discussed in the European Union could be designed to reduce the tax burden on labor by shifting the burden, at least partly, to raw materials, especially non-renewables. It would do so by altering the current price advantage that currently tends to favor virgin over secondary materials. This would increase domestic employment in the high-wage user countries, notably Europe.

### **3.4. Copper in the Environment**

Copper is mobilized from anthropogenic sources to a much greater extent than by natural processes. Globally, natural processes (dust, volcanism, fires) account for atmospheric emissions of about 6 KMT/yr, compared to 35 KMT/yr by anthropogenic processes, of which by far the largest share (23.6 KMT/yr) was due to copper smelting and refining, while another 8 KMT/yr is attributable to coal combustion [Nriagu 1990]. In Europe, another source counted 15.5 KMT of atmospheric copper emissions in 1979, of which half was attributable to copper smelting and refining, and most of the rest was due to fuel (i.e. coal) combustion [Pacyna 1986]. Copper mining by acid leaching undoubtedly contributes significantly to water pollution, with a further contribution from tailings dumps and smelter slag heaps. The leaching rate may increase as rainfall becomes more acid.

### **3.5. Cobalt Sources and Uses**

Cobalt is mobilized in significant amounts by natural processes. The most cited estimate puts biological extraction processes at 30 KMT/y, rock weathering at 10 KMT/y, and fossil fuel (i.e. coal) combustion at 5 KMT/y [Donaldson 1986]. Shedd has modified the Donaldson figures with respect to losses from mining and refining processes. Cobalt recovery varies considerably from mine to mine, and from refinery to refinery, but Shedd estimates an average of 50% taken over all mines and refineries. In this case, for each ton of cobalt produced, another ton is lost in tailings, slag or other products of metallurgical processing [Shedd 1993, p.3].

Cobalt is usually a by-product of copper, although it is also found with some nickel ores (in Australia, Brazil, Canada, France and the Philippines) and with platinum (in South Africa). Zaire recently accounted for over half of recent world output: about 25 KMT in 1989, of the world total of around 45 KMT in that year. However political turmoil has crippled Zairian production. The two largest producers in 1993 were Canada (5738 tonnes) and Zambia (5300 tonnes), followed by Russia (3300 tonnes) and Zaire (2459 tonnes). The world total for 1993 was 22,224 tonnes. Albania was the only active (nickel) mine source in Europe, though production has effectively ceased.

Zaire was formerly the largest cobalt refiner, as well as the largest source of ore, followed by the (former) USSR. However in 1993 the major refiners were Russia (4000 tonnes),

Zambia (3700 tonnes), Canada (2695 tonnes), Norway (2414 tonnes) and Finland (2200 tonnes). The world total for 1993 was only 16,893 tonnes, sharply down from 1989. Some of the Norwegian output is derived from Canadian concentrates. The Finnish refineries obtain concentrates and semi-refined materials from Australia, New Caledonia and Indonesia. There is a nickel-cobalt refinery in France (Le Havre) that produces around 150 tonnes per year from New Caledonian nickel ores.

The largest end-use of cobalt is for high temperature resistant "superalloys" (usually with nickel and chromium) notably in jet engines. Of 7065 MT consumed in the U.S. in 1989, 2813 went for this purpose. Consumption for this purpose in 1993 was slightly lower (2614 tonnes). This use had been increasing for several decades, but now appears to have peaked. Cemented carbides for cutting tools accounted for 569 tonnes in 1993. Magnets — mainly AlNiCo and Samarium-Cobalt — accounted for 860 MT in 1989 and 629 tonnes in 1993 [USBuMines 1993].<sup>3</sup> Chemical uses of cobalt included catalysts (935 tonnes in 1993), driers for paint (732 tonnes in 1993), pigments (193 tonnes) and several uses for coloring and decolorizing ceramics and glass. Some cobalt is consumed for animal feeds. Superalloys and magnets are recoverable. Catalysts, pigments, driers, animal feeds and other chemical uses and carbide cutting tools are likely to be dissipative. The European consumption pattern is probably similar to the U.S. pattern. Losses from dissipative uses appear to average about 50% of total consumption, or about 10 KMT for the world, which is far less than other sources of cobalt in the environment [Shedd 1993 Table 1].

Cobalt is undoubtedly a "strategic" mineral, given the small number of producers and the importance of its uses. In the circumstances it is perhaps surprising that the recycling rate is so low. Despite relatively high recent prices, only about 20-25 % of U.S. cobalt consumption is recovered from purchased scrap [Shedd 1993]. However, unless cobalt turns out to have unexpectedly major environmental impacts, the obvious strategy is to increase the cobalt recovery rate from copper, nickel and/or lead mining.

### 3.6. Arsenic Sources, Uses and Losses

Arsenic constitutes only about 2 parts per million of the earth's crust (compared to 58 ppm for Cu). It is found in sulfide minerals associated with copper, zinc, lead and gold ores, but predominantly with copper. About 15% of all commercial copper, zinc, lead and uranium ores are classed by the Bureau of Mines as arsenical, with an average Cu/As ratio of 50:1 (in non-arsenical copper ores the ratio is 500:1). In smelters, arsenic is normally allowed to remain in the concentrator tailings, since it has a low commercial value. It is recovered (if at all) at copper smelters<sup>4</sup> in a preliminary roasting/sublimation stage, where there are also significant losses to slags and flue dusts, which are typically dumped on land. Flue dusts constitute a major disposal problem, although methods of converting the contained arsenic to an insoluble form are under investigation [USBuMines 1989 p. 125]

World mine production of arsenic in 1993 was 47 KMT, down from 57.91 KMT in 1989. Major European producers in 1989 were:

	1989	1991
Belgium	3.50	3.00
France	7.00	3.00
Germany	0.36	0.36
Portugal	0.18	0.20
Sweden	10.00	2.50
<b>Total</b>	<b>21.04</b>	<b>9.06</b>

In the case of Belgium the arsenic is a by-product of copper refining, mainly from Zaire. In the case of France, the arsenic appears to be a by-product of nickel-cobalt ore refining, from New Caledonian ore. In the case of Sweden, the source of the arsenic is a very high arsenic copper ore. Production from all three countries has declined sharply since 1989. Figures for 1991 were: Belgium 2.5 KMT; France 3, Sweden 2.5 KMT MT. By 1993 Belgian output was down to 2 KMT and Swedish output was only 0.5 KMT. Declining demand is the probable explanation.

Arsenic is processed into a number of chemical forms (*Figure 3.3*). Metallic arsenic (produced only in China) accounts for only 3% of total use. In the U.S., 70% of total demand is now for wood preservatives, in the form of chromated copper arsenate (CCA). See *Figure 3.4*. (This use is discussed further in *Chapter 4, Chromium*.) Herbicides and desiccants account for most of the rest. Sodium Arsenite,  $\text{NaAsO}_2$  is still used as a domestic insecticide. Arsenic Acid,  $\text{H}_3\text{AsO}_4$  is used as a desiccant for cotton plants (to remove their leaves prior to mechanical harvesting by cotton strippers). There has been increasing use since the 1960's. The European consumption pattern is almost certainly similar, except that cotton is not grown in Europe.

Other minor uses of arsenic include: glass and ceramics, where arsenic has long been used as a decolorant and fining agent (~5%); an additive to chicken feed (~1%); treatment of syphilis and African sleeping sickness (~1%); alloying agent for lead in lead-acid batteries (to strengthen posts and grids) and to increase the tensile strength of copper (~3%).

A use that is still extremely small, but which is growing rapidly, is in semi-conductor manufacturing: specifically, gallium arsenide, is now used for preference in very fast microprocessors and solid-state laser devices. The manufacturing process itself is a potential source of very toxic arsenic emissions (e.g. arsine) but the long-run problem is likely to arise from the difficulty of recycling electronic devices and their consequent buildup in landfills. However, compared to others, this problem is minor. Moreover, it seems unlikely that electronic uses could ever account for more than a small percentage of global arsenic supply. This use should therefore be encouraged as a way of "soaking up" arsenic that is otherwise likely to be dissipated in other less benign ways. The environmental impact of arsenic flows is discussed in *Section 3.7* below.

### 3.7. Arsenic in the Environment

Obviously, if arsenic is not recovered from the copper ore during the refining process, it must remain with the tailings or slag, or be lost to the air. Unfortunately, arsenic is rather volatile and any arsenic that enters a furnace is likely to be vaporized. According to another source

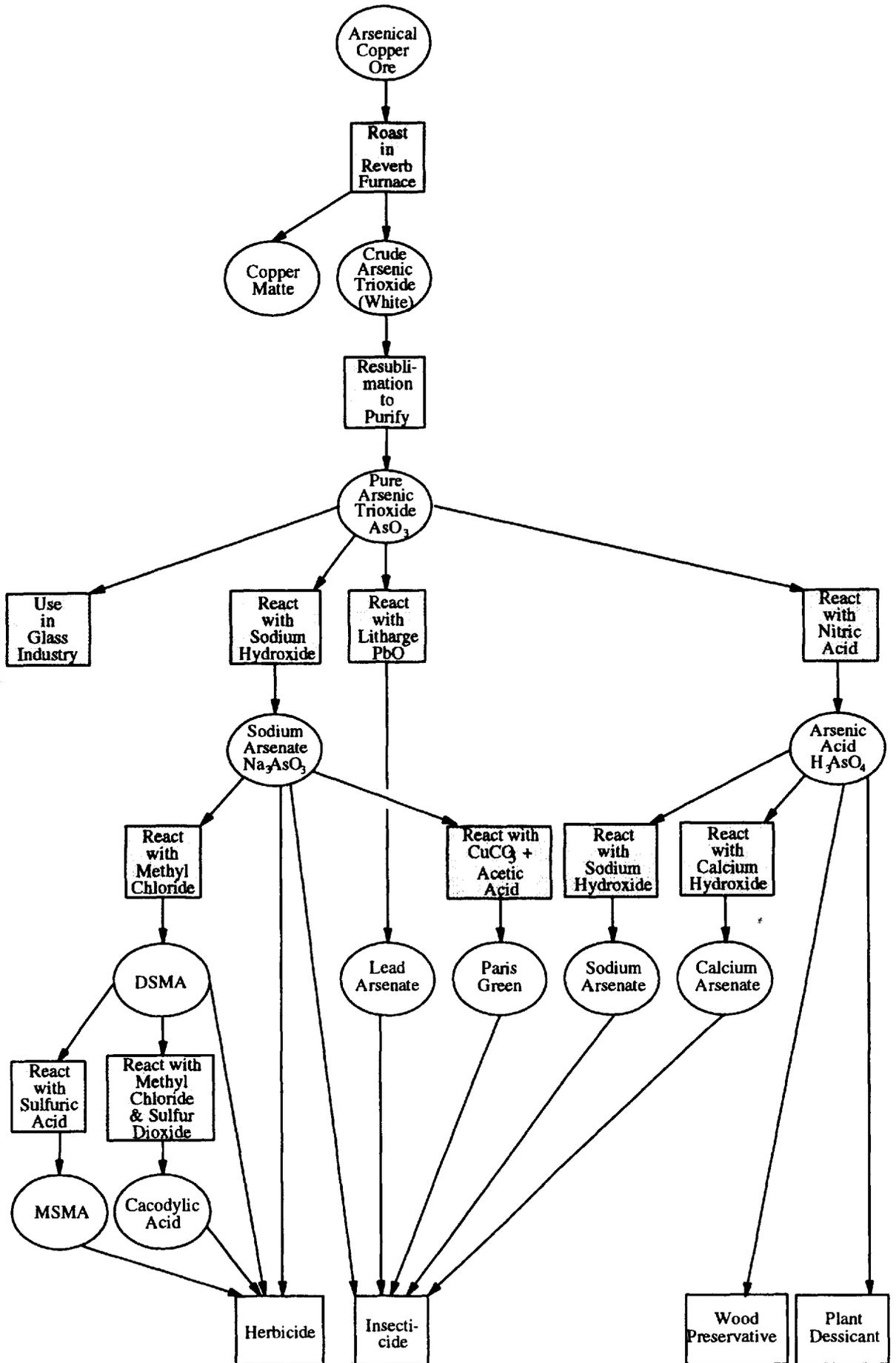


Figure 3.3. Arsenic process-product flows

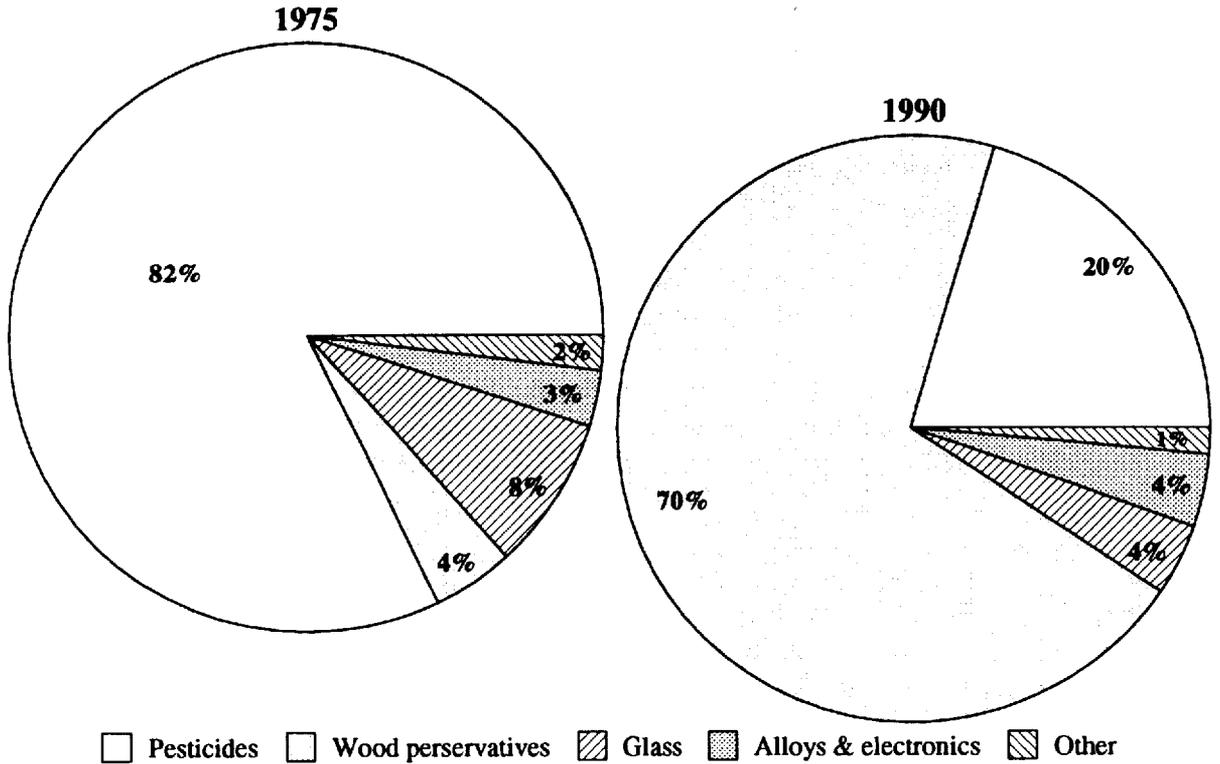


Figure 3.4. U.S. consumption of arsenic by end-use 1975 & 1990 (%)   
 Source: [Roskill, "Arsenic", 1992]

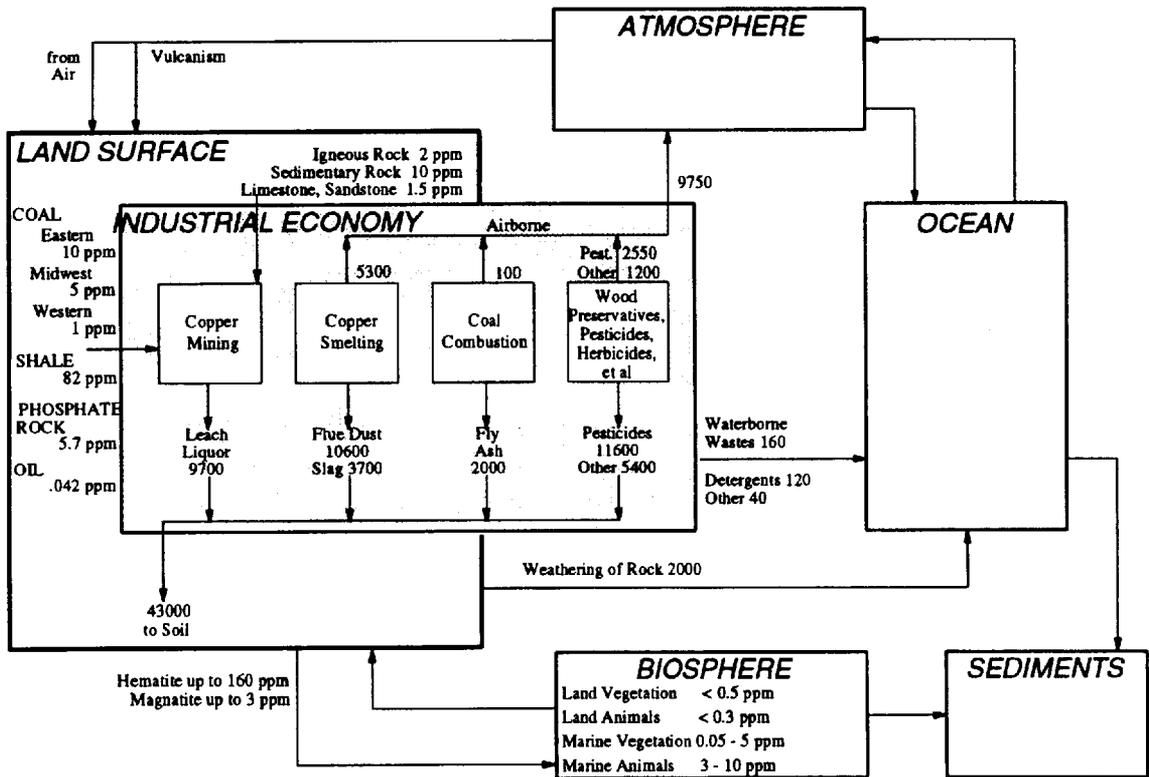


Figure 3.5. Global arsenic cycle 1980 (metric tonnes)

to the U.S. alone) 9.7 KMT/yr was lost in leach liquor from copper mining, about 5.3 KMT/yr was vaporized in copper smelting, 10.6 KMT/yr was captured as flu dust (and dumped) while 3.7 KMT/yr was incorporated in copper smelter slags [Ayres *et al* 1988]. By contrast fly ash from coal combustion contained 2 KMT/yr of arsenic, of which only 100 tonnes was emitted to the air and the remainder was captured by electrostatic precipitators and dumped on land. See *Figure 3.5*.

More recently, Nriagu has estimated global atmospheric arsenic emissions from metal — mostly copper — mining, smelting and refining at 12.4 KMT/yr, compared to 2.2 KMT/yr from coal combustion, 2 KMT/yr from manufacturing processes and 2.3 KMT/yr from commercial uses, transportation and waste incineration [Nriagu 1990]. Evidently atmospheric emissions alone are comparable to consumptive uses. Anthropogenic activities account for 19 KMT compared to 12 KMT for natural processes such as vulcanism and forest fires [ibid]. Within Europe, Pacyna has accounted for 6.5 KMT/yr in airborne emissions from all anthropogenic sources, of which copper/nickel smelting and refining accounted for 4.5 KMT/yr and other non-ferrous smelting and refining accounted for another 1.2 KMT/yr and fuel combustion the rest [Pacyna 1986]. Emissions to the North Sea have also been estimated at 2.2 tonnes/day from rivers as compared to 0.63 tonnes/day from atmospheric deposition, for a land/water ratio of 3.5 [Pacyna 1986]. The major problem of arsenic in the environment is its inherent mobility.

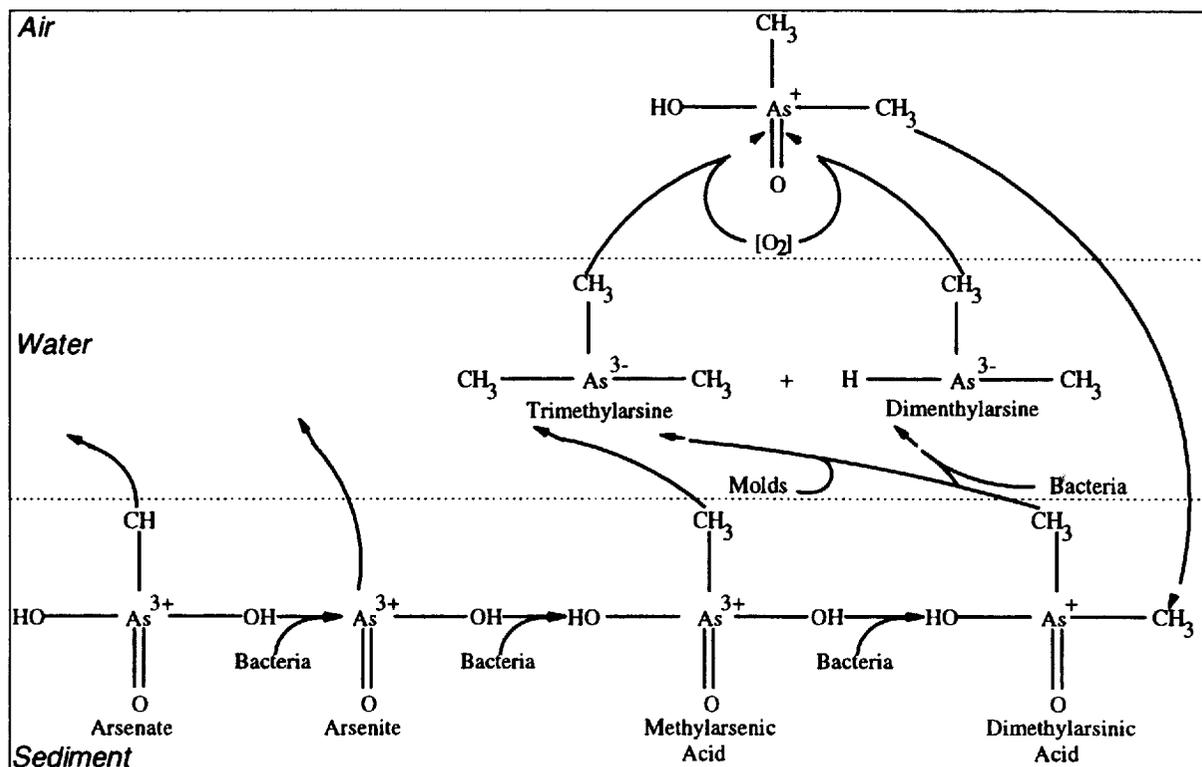


Figure 3.6. Biological cycle for arsenic. Source: [Wood 1974]

Arsenic has a comparatively low boiling point, so that it is relatively easily vaporized. Arsenic is also metabolized by some anaerobic bacteria in soils and sediments. These bacteria produce methylated arsenic compounds, some of which are water soluble, others being volatile. As yet

there is no authoritative description of the biological "arsenic cycle", but *Figure 3.6.* illustrates some of the possible transformations and fluxes.

The point is that once arsenic is released into the environment, it accumulates and moves. It may wash into the sea, but it can also escape back into the atmosphere. There may be mechanisms for permanent immobilization and "burial", but we do not know what they are, still less the rate at which this may take place, if it does.

For this reason, even in the absence of quantitative evidence of toxic effects on human health, it seems foolhardy to allow continued dissipation of arsenic into the environment, where it continues to accumulate.

### 3.8. Silver Sources, Uses and Losses

Silver is a relatively rare metal. It constitutes about 0.2 parts per million, by weight, of the earth's crust. Silver (and gold) are often found in association with other non-ferrous metals, such as lead, copper and zinc. Even high-grade silver ores contain very little silver – typically a few ounces per ton of ore. Thus, of the order of ten tonnes of non-ferrous metal ores (Cu, Zn, Pb, Mo) must be moved and processed to yield one kg of silver. All commercially important silver minerals at present are sulfides.

About two-thirds of silver output is now obtained from copper and zinc ores (in the U.S.), with the remaining third from ores classified by the Bureau of Mines as silver ores [USBuMines 1975]. The latter are primarily underground. Gold is usually a minor by-product in all cases. Silver is recovered commercially from copper during the final electrolytic refining stage. (In the case of zinc and lead, it is recovered at the smelting stage). Silver ores *per se* are first treated by cyanidation. (Mercury was used for the same purpose in the 19th century). The silver and gold are precipitated from the cyanide solution by adding zinc dust, leaving a silver-gold alloy called dore metal.

In 1993, world mine production was 14,900 tonnes. In the U.S. 1700 tonnes of silver were recovered from ores. In 1989, 2007 tonnes were recovered from 405.7 MMT of non-ferrous ores, of which 230.56 MMT were copper ores. The biggest producer in the world is Mexico (2200 tonnes), followed by the U.S. (1700 tonnes). Others producing more than 1000 tonnes, in order, were Peru, Australia and Canada. Europe produced declining and minor quantities. Figures for 1989 were Spain (350 tonnes), Sweden (195 tonnes), Italy (93 tonnes) and Germany (70 tonnes).

Silver is used, today, primarily for its chemical and electronic properties. In the past, this was not the case; most silver was mined for its own sake and was used in metallic form as bullion (backing for currency), coinage, or jewelry, "silverware" and for objets d'art. Except for sterling silverware, plateware, jewelry and coinage, the uses are largely dissipative, although some spent silver batteries and wastes from film processing facilities can be recycled. Consumptive uses of metallic silver have included solders, brazes, plated bearing surfaces, electrical contacts, and silver gauze catalysts, silver impregnated glass used for protective

spectacles. Metallic silver is relatively unreactive except in the presence of sulfur, and most silver salts are quite insoluble.

Chemical uses include pharmaceuticals (especially silver nitrate), which are still used to treat warts, boils, bites, small growths, ophthalmia, gastric ulcers, gonorrhea and chronic dysentery. Silver chemicals are also used in specialized electric batteries (e.g. silver-zinc cells), and photographic films. By far the most important chemical use today is in photography, with silver based batteries and catalysts distant runners up.<sup>5</sup>

Photographic film is a multi-layer material consisting of a colloidal dispersion of silver halide (chloride, bromide, chloro-bromide or iodide) grains in a special gelatin that performs the functions of mechanical binder, and sensitizer. The gelatin is usually supported by a paper backing. The manufacturing process is extremely complex and many of the details are proprietary. However, the starting point is a solution of sodium or potassium halides and gelatine. To this is added silver nitrate ( $\text{AgNO}_3$ ) and ammonia are added at 40°C-50°C and the silver halides grains are precipitated under suitable conditions.

In the "black and white" era much of the developing was done in small laboratories and significant quantities of silver-containing chemicals were discarded. Color film was, and is, more likely to be processed in a centralized facility where silver recovery is practicable. The movie and publishing industries are major users of film, and much of this is recycled in small 'film stripping' facilities to recover silver. Thus silver loss in photography has not by any means been proportional to total film production. However, consumptive — and dissipative — usage has ranged around 30% of net industrial consumption of silver (in the U.S.) since the 1950's.

Silver losses to the environment from mine tailings and slag are not significant, since most of the silver is recovered. Most losses are probably attributable to photographic film developing (especially in smaller facilities) and disposal of used film in refuse, to landfills and incinerators. Use and disposition of other silver-based products such as mirrors, batteries, solders, brazes, and electronic equipment can be considered to be secondary sources. Silver is also dispersed into the environment via the combustion of coal and oil, but to a very minor degree.

Silver is not one of the most important environmental hazards, though neither is it negligible. But it is a useful illustration of an important point. Silver is 50-100 times more valuable than copper, for instance (roughly \$4 per oz., as compared to \$0.40-\$1.20 per pound), and yet dissipative losses remain significant. This is because the amount of silver required to perform a useful and economical valuable function can be extremely small. Thus, for many metals used in small quantities for specialized purposes, to achieve anything close to 100% recycling by means of market forces alone is, at best, a very distant prospect.

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## Endnotes(3)

1. Some material in this chapter was adopted from Robert U. Ayres, and others *An Historical Reconstruction of Major Pollutant Levels in the Hudson-Raritan Basin 1800-1980* [Ayres *et al* 1988]. We are grateful for helpful criticisms and suggestions from D.L. Edelstein and an anonymous reviewer of the U.S. Bureau of Mines, and Prof. John E. Tilton of the Colorado School of Mines. They are not responsible for any remaining errors or misunderstandings on our part, nor do they necessarily agree with our views.
2. To be sure, the U.S. is actually an importer of arsenic despite its large copper mining and smelting sector. This is because U.S. copper ores are relatively low in arsenic and imports are cheaper than recovery. The only arsenic recovery facility in the U.S. (Tacoma Washington) was shut down a few years ago, partly for economic reasons and partly for environmental reasons. However, unrecovered arsenic must therefore remain in tailings, slag, baghouse dust and other process wastes.
3. In 1981 it was estimated that magnets accounted for 16% of worldwide cobalt use [Voigt 1982]. German industry consumed 210 MT of cobalt for magnets in 1981.
4. Since 1973 only one U.S. smelter recovers arsenic commercially (ASARCO, at Tacoma, WA). This plant processes arsenical ores and flue dust from other U.S. smelters.
5. Important chemical processes (mostly partial oxidation) utilizing silver-based catalysts include the following:
  - acetaldehyde from ethanol
  - acetone from isopropanol
  - acrylonitrile from propylene
  - ethylene oxide from ethylene
  - formaldehyde from methanol

Silver use for catalytic purposes apparently peaked in 1976 or 1977 at a level of 9 million oz. per year (net). It would appear that net consumption, in this case, is tantamount to loss.

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