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Toxic heavy metals: Materials cycle optimization

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ABSTRACT Long-term ecological sustainability is incompatible with an open materials cycle. The toxic heavy metals (arsenic, cadmium, chromium, copper, lead, mercury, silver, uranium/plutonium, zinc) exemplify the problem. These metals are being mobilized and dispersed into the environment by industrial activity at a rate far higher than by natural processes. Apart from losses to the environment resulting from mine wastes and primary processing, many of these metals are utilized in products that are inherently dissipative. Examples of such uses include fuels, lubricants, solvents, fire retardants, stabilizers, flocculants, pigments, biocides, and preservatives. To close the materials cycle, it will be necessary to accomplish two things. The first is to ban or otherwise discourage (e.g., by means of high severance taxes on virgin materials) dissipative uses of the above type. The second is to increase the efficiency of recycling of those materials that are not replaceable in principle. Here, also, economic instruments (such as returnable deposits) can be effective in some cases. A systems view of the problem is essential to assess the cost and effectiveness of alternative strategies.

The mining and smelting of toxic heavy metals can be traced back thousands of years. However, production has grown rapidly since the industrial revolution (Fig. 1). This is due, in large part, to the fact that copper, lead, silver, tin, zinc, and other heavy metals tend to be easy to identify (often they are brightly colored sulfide minerals), relatively easy to smelt, and relatively easy to work.

It is helpful, at this point, to introduce a simple taxonomy of economic activities, as follows:

(i) Primary sectors are concerned with extraction of raw materials (mining, quarrying, agriculture, logging), physical processing to concentrate crude materials and dispose of wastes (beneficiation of ores, washing of coal, distillation of crude petroleum, debarking of logs, threshing of grain, peeling and coring of fruits, etc.), and thermal or chemical processing (roasting, smelting, calcining, electrolytic or oxygen refining, alloying, dehydrogenation, refining, pulping of wood, cooking or baking of food products, etc.). The outputs of the primary sectors are finished materials, including fuels, commodity chemicals, and electricity.

(ii) Secondary sectors are concerned with conversion (shaping, forming, joining, weaving, assembly, coating, painting or dyeing, printing, etc.) of finished materials into manufactured products, including structures. The so-called “fine chemicals,” pharmaceuticals, cosmetics, and other such products may also be regarded as secondary.

(iii) Tertiary sectors generate services, not products. The services may be produced either by persons (e.g., nursing or teaching) or by means of specialized material products or

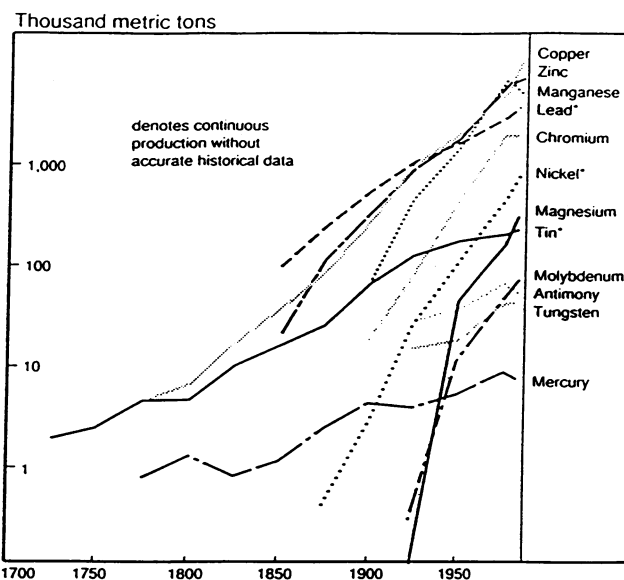


FIG. 1. Annual worldwide production of selected metals from 1700 to 1983 [reproduced from ref. 1 with permission (copyright Wiley & Sons)].

infrastructure. Examples of the latter include transportation and communications.

This scheme is elaborated in Fig. 2. It is intuitively clear that primary production activities are intrinsically much “dirtier” than secondary activities, which are (in turn) dirtier than tertiary activities. This is because primary activities involve the separation of desirable ores from some mineral matrix, and thence from chemical combinants, and the discard of whatever is unwanted. While the first activity is geographically limited to the region of the mine, the quantities of materials that must be moved are extremely large (with correspondingly large energy and power requirements (see Table 1).

The discarded materials are, by definition, wastes and/or pollutants. In the case of open-pit mining, especially, the resulting pollution problems can be quite severe. Waste and pollution problems are also associated with all stages of materials processing, but the largest volumes of waste emissions are created by the beneficiation (concentration) and smelting of ores and the combustion of coal. In addition, significant quantities of heavy metals are released into the environment as a result of the processing of phosphate rock, the manufacture of cement, and the smelting of iron ore. Global annual average estimated atmospheric emissions of toxic metals from various sources are summarized in Table 2. Anthropogenic emissions now dominate natural sources by an order of magnitude or more in most cases.

Abbreviation: PVC, poly(vinyl chloride).

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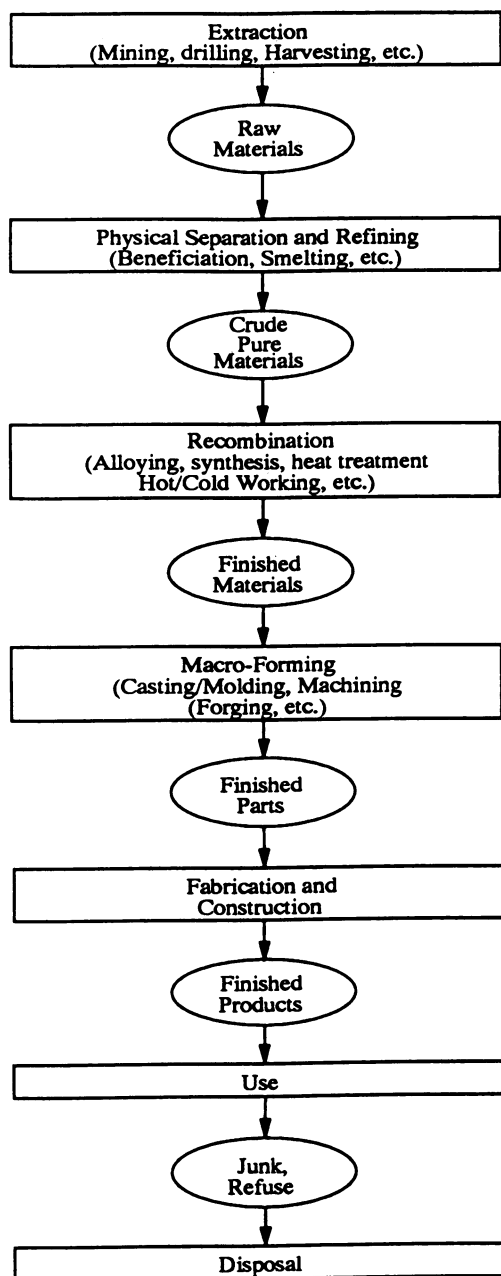


FIG. 2. Materials-process flow.

However, there is a major caveat to these generalizations. In fact, there are also major flows of toxic heavy metals into the environment resulting from inherently dissipative use. Tetraethyl lead added to gasoline is the classic example of such a dissipative use, fortunately now sharply reduced in the U.S. (though still high and even increasing in other parts of the world). Other dissipative uses include paints and pigments, flocculants, stabilizers, antioxidants, lubricants, herbicides, fungicides, algicides, insecticides, antiseptics, preservatives, and medicinals. Examples are discussed below.

Metallic products are theoretically amenable to recovery and recycling. Yet, the actual recycling rate is surprisingly low in some cases. In the case of chromium, secondary recovery in 1983 contributed 23.4% (up considerably from the early 1970s). In the case of copper, lead, mercury, and zinc, old scrap accounted for 22%, 45%, 35%, and 7.6% of domestic demand, respectively, in 1983 (4). Internal recycling within the metallurgical sector accounts for the somewhat higher figures shown in Table 3. The especially low figure for zinc reflects the fact that major uses of zinc are for zinc

Table 1. Gross quantities (tons) of material handled per ton of metal

Metal	Tons
Copper, surface	550
Copper, underground	337
Lead, underground	30
Zinc, underground	31

Data are from ref. 2.

plating (galvanizing) and zinc chemicals. Recovery for such uses is inherently very difficult.

Conservation of mass implies that the difference between what is produced and what is recycled must be lost or dissipated. Losses to the environment due to inherently dissipative consumptive uses are estimated directly (for the U.S.) in Table 4. Uses and emissions of the major toxic heavy metals are summarized briefly later. The only true "sink" for heavy metals released into the environment is the sedimentary accumulation at the bottom of the oceans. Metallic emissions to the atmosphere have a short lifetime, averaging a few days at most. Because of this, metals do not accumulate in the atmosphere and do not (in general) travel very far from the point of origin. However, particulate fallout or emissions directly to the land surface (or to sediments in lakes and rivers) have a much longer lifetime, ranging from a few hundred years to several thousand years (Table 5). Because of the short distance of airborne travel, metallic emissions tend to fall out mainly on the land surface. Here they may be metabolized by bacteria and incorporated into the food chain. They reach the oceans mainly via runoff from the land. The relative importance of land-based and direct atmospheric contributions to the North Sea are shown in Table 6.

The buildup of toxic heavy metals (arsenic, cadmium, copper, chromium, lead, mercury, etc.) in the biosphere—topsoil, river bottom sediments, estuarine sediments, and groundwater—is a direct consequence of the extraction and use of toxic heavy metals for human activity. These materials have a place in our industrial metabolism, so to speak. However, except in trace amounts, they are generally harmful to the biosphere.

Thus, sustainability of the biosphere in the long run is not compatible with a buildup of these materials in the soils and sediments. This clearly implies that extraction of virgin ores of the toxic heavy metals must be drastically reduced, and many industrial processes must be changed to eliminate or recover and utilize most, if not all, waste products. It follows that inherently dissipative uses of material goods—especially toxic, mutagenic, or carcinogenic ones—must be curbed; materials must be increasingly remanufactured or otherwise recycled.

Table 2. Estimated annual global emissions of selected metals to the atmosphere, circa 1980

Metal	Human activity metric tons $\times 10^{-3}$	Natural activity, metric tons $\times 10^{-3}$	Human/natural activity ratio
Lead	2000	6	333
Zinc	840	36	23
Copper	260	19	14
Vanadium	210	65	3
Nickel	98	28	4
Chromium	94	58	2
Arsenic	78	21	4
Antimony	38	1	38
Selenium	14	3	5
Cadmium	6	0.3	20

Data are from ref. 3.

Table 3. Scrap use in the United States

Material	Total consumption, short tons $\times 10^{-6}$			% total consumption in recycled scrap		
	1977	1982	1987	1977	1982	1987
Aluminum	6.49	5.94	6.90	24.1	33.3	29.6
Copper	2.95	2.64	3.15	39.2	48.0	39.9
Lead	1.58	1.22	1.27	44.4	47.0	54.6
Nickel	0.75	0.89	1.42	55.9	45.4	45.4
Steel/iron	142.40	84.00	99.50	29.4	33.4	46.5
Zinc	1.10	0.78	1.05	20.9	24.1	17.7
Paper	60.00	61.00	76.20	24.3	24.5	25.8

Data are from ref. 5.

Need for Systems Analysis and Modeling

Up until now, the industrial need for these metals has seldom been questioned, still less examined analytically. What are the trade-offs? Why not recycle more? What would it cost society if dissipative uses of toxic metals were to be banned or strongly discouraged by other means, such as emissions taxes? There is a need for a comprehensive systems analysis of the toxic heavy metals, with particular emphasis on the materials cycle. As an example, consider the case of copper, as depicted schematically in Fig. 3.

To illustrate the importance of looking at the heavy metals problem from a systems perspective, suppose for the sake of concreteness that improved recycling technologies for copper could increase the secondary fraction from old scrap by, say, 20% with a corresponding reduction in primary copper production. In 1983, secondary copper production from old scrap in the U.S. amounted to some 350 thousand tons (4). A 20% increase would be 70 thousand tons; the same amount would be deducted (by assumption) from primary copper production—a reduction of 6%.

Arsenic is a normal component of copper ore ($\approx 0.65\%$); the potential U.S. production of arsenic in a typical recent year, 1983, would have been >7200 tons, based on a U.S. copper mine output of just over 1.1 million tons of primary copper (4). Of this amount, only 1000 tons, or 12.8%, was actually recovered and sold as such (4). (Most of the arsenic actually consumed in the U.S. was imported from abroad.) The remainder of the arsenic in the copper ore was lost in the mining or refining processes. For instance, it is estimated that primary emissions to the atmosphere from copper smelters in the mid-1970s was 3.5 lb/ton, or 1650 tons. (Hopefully, this

has been reduced in recent years.) The rest was dispersed in mine tailings and smelter slags.

The impact of a hypothetical increase in copper recycling on actual domestic arsenic output is indeterminate, since copper ores vary and it depends on which copper mines and refineries were cut back. However, assuming average ore composition throughout the industry, based on the arsenic data already noted above, this would imply a 6% cut in domestic U.S. arsenic production (i.e., from 1000 to 940 tons) and also a 6% cut in arsenic losses to the environment during copper mining and smelting, or 370 tons (6% of 6200 tons). In addition to the reduced emissions of arsenic, nearly 11 million tons of copper mine tailings would not have to be dumped near the mines; 42 thousand tons less of by-product sulfur would be recovered; 10 trillion British thermal units (0.01 quad) of fuel would be saved, along with 167 megawatt hours of electric power (see Fig. 3). Other waste emissions associated with primary copper smelting and refining would also be reduced, although these would have to be balanced against waste emissions from secondary copper melting and refining.

Several generic questions now arise quite naturally. First, given the by-product and coproduct relationships determined by natural ore compositions, existing process technology, and current demand patterns (and prices) for the eight major toxic metals listed above, what is the least-cost configuration of mining and processing technologies? Second, what configuration of technologies would minimize irreversible dissipation of toxic metals into the environment? Third, how does the environmentally optimum solution (assuming fixed demand) compare with the economically optimum solution, both in terms of cost and in terms of aggregate environmental loading? What are the trade-offs between the two objective functions? How do the results change as the pattern of final demand is varied? How would aggregate environmental waste emissions respond to various hypothetical modifications to the demand picture, such as emissions taxes and/or severance taxes? Only with the help of a well-developed materials-process-product engineering-economic model could such questions be answered convincingly. Meanwhile, one can only suggest possibilities.

Closing the Materials Cycle

Undoubtedly the most hazardous of all heavy metals is plutonium, a man-made by-product of uranium fission. Apart from its military potential, it is extremely toxic and carcinogenic. However, an adequate discussion of this problem is inseparable from

Table 4. Emissions from consumptive uses: Heavy metals in the United States 1980 (tons)

Use	Silver	Arsenic	Cadmium*	Chromium	Copper	Mercury†	Lead	Zinc
Metallic (except coatings and electrical)	0.83	0.04	0.04	151.8	11,074		1249	514
Protective coverings								
Plating and coating	a		136.1	155.7				8778
Paints and pigments			116	6490			48,500	77,750
Electrical								
Batteries and equipment	0.15	1.97	7.81			195.91	8510	63
Other electrical uses	0.67					17.52		
Chemical								
Industrial catalysts, reagents, etc.	7.6	492		1297	4222	412.1		2508
Consumer uses; additives, etc.	48		29	3890				18,622
Biocidal poison								
Agricultural (pest-, herb-, fungicides)		2950			1560	16		188
Nonagricultural (pesticides except medical)		5901		1038		236		251
Medical, dental, pharmaceutical	1.51	19.7				8.36		1003
Miscellaneous N.E.C.	0.45		0.98	2141		6.96	1329	
Total	60	9364	290	11,659	15,452	893	56,900	109,670

Data are from ref. 6. Included in first column.

*1979.

†1977.

Table 5. Residence times of metals in environmental compartments

	Residence times, yr				
	Arsenic	Selenium	Mercury	Cadmium	Lead
Atmosphere	3.0×10^{-2}	3.0×10^{-2}	1.0×10^{-1}	2.0×10^{-2}	
Land	2.4×10^3	4.6×10^3	2.8×10^2	3.0×10^3	3.0×10^3
Oceans	9.4×10^3	2.3×10^3	8.8×10^2	2.1×10^3	
Sediments	99.8×10^6	93.5×10^6	90.8×10^6	99.8×10^6	99.0×10^6

Data are from ref. 1.

the linked problems of nuclear weapons and nuclear waste disposal. I will not pursue the subject further here.

The dissipative use of lead was mentioned above. Tetraethyl and tetramethyl lead have been used in enormous quantities as an octane enhancer for gasoline since the early 1930s. It is still used for this purpose in most of the world. After combustion, lead from gasoline accumulates in the motor oil (much of which leaks or is dumped) or is emitted into the air, where it gradually falls out, mostly along the roads and highways, or in the cities. Some is washed into streams; the rest accumulates in the soil. Its use in the U.S. has been virtually eliminated since the early 1970s, and unleaded gasoline is now available throughout western Europe and in Japan, although most vehicles still use the leaded variety. However, the elimination of lead from gasoline was not cost-free. Partial substitutes for tetraethyl lead are now used (e.g., alcohols and aromatics); yet octane levels have nevertheless declined significantly, requiring lower engine compression ratios and *ceteris paribus* reduced fuel economy. This has further environmental impact.

In the past, large quantities of lead were used in insecticides (e.g., lead arsenate) and lead-based paints (white lead, red lead). Lead paints were once used for many purposes—interior and exterior—and have continued to be used until recently for the protection of steel surfaces (e.g., bridges). Paint is a colloidal suspension of solid pigments in a liquid medium (oil or water). The medium dries and hardens, but eventually through oxidation, deterioration caused by ultraviolet radiation, and physical wear, the painted surface cracks, flakes, and becomes powdery. Thus, the millions of tons of lead compounds that were once used for paints have long since been dispersed into the environment. Some of it is still in old buildings; much is to be found in landfills, where demolition wastes have been dumped. But a great deal has been more widely dissipated into soils and sediments.

To close the materials cycle for lead, a combination of very high severance taxes on lead from the mine, and/or a worldwide ban on dissipative uses such as gasoline, paint, insecticides, and most other lead-based chemicals will eventually be necessary. The sharply higher prices resulting would also enable secondary lead from low melting alloys and other metallic uses to be recovered more economically and hence more efficiently than is now the case. High severance taxes on copper, chromium, and zinc would also be appropriate, for much the same reason cited above—to encourage recover, reuse, and recycling.

Mercury is a very toxic metal whose uses are now almost entirely dissipative. It is not a by-product. In the past, it was used for medical purposes: as an antiseptic, preservative (e.g., to preserve felt hats or to keep seed grain from rotting), as submarine ballast, to protect ships' hulls from barnacles, to protect interior paint from mold and mildew, to protect paper pulp from bacterial attack, as a red pigment, for thermometers, for the mining of silver and gold, as a dental amalgam. It is still used as a catalyst for several chemical processes, in electrical switches, in chloralkali manufacturing (to the so-called mercury cell), and in two kinds of miniature primary cells. Alkaline cells, sold by the hundreds of millions for flashlights, cameras, "walkmen," radios,

smoke detectors, etc., normally contain $\approx 1\%$ mercury by weight. It can be eliminated, but cell life is cut by 25% or so. Tiny "button" batteries, used for hearing aids, contain a much higher percentage of mercury.

Virtually no mercury is now recycled, although hearing-aid batteries could be recycled fairly easily by the simple expedient of requiring a high returnable deposit (or trade-in) for the return of old batteries when new batteries are purchased. Most dissipative uses could be banned quite easily with little or no economic loss.

It was noted above that a number of most toxic metals (e.g., arsenic, bismuth, cadmium, thallium) are rarely mixed for their own sake but occur as by-products of copper, lead, or zinc mining. This means that there are two possibilities: (i) they will necessarily be incorporated in and dispersed in mine tailings, smelter dust, or slag, or (ii) they will be separated, refined, and incorporated in "final" products of some sort. There is a considerable incentive to find economic uses for these by-product metals. Arsenic and cadmium are good examples. (In fact, many of the modern uses of arsenic were developed by Swedish researchers, trying to make a virtue of necessity: Swedish copper ore is unusually high in arsenic.)

Of the arsenic consumed in final products, almost all was in products ultimately dissipated into the environment. Only a small fraction is used in metal alloys (mainly with copper or lead) or ceramics. Indeed, the major economic uses of arsenic actually exploit its toxicity to various forms of life. In the past, it was widely used as an insecticide (e.g., lead or zinc arsenates). The largest single use today is for wood preservatives. Herbicides and plant desiccants account for most of the rest. Arsenic is, therefore, building up slowly but inexorably in the environment, where it is easily metabolized by bacteria and further dispersed in gaseous form.

If dissipative uses of arsenic were banned absolutely, the arsenic associated with copper mining would have to be disposed of permanently, perhaps by embodiment in a ceramic or glassy matrix. (The problem is comparable to that of disposing of nuclear wastes.) Metallic uses—such as gallium arsenide—might still be feasible, although the problem of recovery of electronic materials remains unsolved to date. Needless to say, the cost of primary copper would rise somewhat, thus encouraging more recovery and recycling of old copper scrap.

Similarly, cadmium is a minor component of zinc ore ($\approx 0.42\%$ in the U.S.); potential U.S. production is therefore

Table 6. Land-based and atmospheric contributions to heavy metals in the waters of the North Sea

Metal	Land-based, tons/day	Atmospheric, tons/day	Relative contribution, land/atmospheric
Arsenic	2.2	0.63	3.5
Cadmium	0.68	1.56	0.4
Chromium	18.3	1.83	10.0
Copper	12.9	10.8	1.2
Lead	17.9	8.0	2.2
Mercury	0.18	0.14	1.3
Nickel	11.1	4.3	2.6
Zinc	86.3	19.2	4.5

Data are from ref. 1.

≈1300 tons, based on 1983 primary zinc refinery output of just over 300 thousand tons (4). Actual production of cadmium was 1052 tons, or ≈91% of the potential. Even as a minor contaminant of zinc ore, cadmium finds its way into commercial grades of zinc oxide (used in huge quantities in tire manufacturing) and, through tire wear, into road dust. Cadmium was once used extensively for red and yellow pigments (still used in some ceramics and glasses), and for metal plating (in competition with zinc and nickel). It has some applications as an alloying element. Cadmium is still used as a stabilizer for the plastic polyvinyl chloride (PVC), whence it contaminates incinerator ash when PVC is incinerated.

The economic reason for the high rate of cadmium recovery at present is that cadmium currently has an important and growing market in the manufacture of small rechargeable

nickel/cadmium cells. This use is harmless in itself, although the vast majority of such batteries are ultimately discarded and find their way into landfills. The ultimate fate of the cadmium accumulating in landfills is unclear, although it seems to be temporarily safe. The only secondary cadmium recovered at present is from new scrap generated during cadmium battery production, some remelting of cadmium-containing special alloys, and a small amount recovered from pollution control devices at cadmium processing facilities (e.g., battery plants). A practical means of recovering and recycling cadmium from batteries is increasingly needed.

Silver is still mined for its own sake but is now almost entirely produced as a by-product of copper, lead, or zinc mining. Its metallic uses—jewelry, cutlery, coinage—are well known and comparatively harmless. However, silver

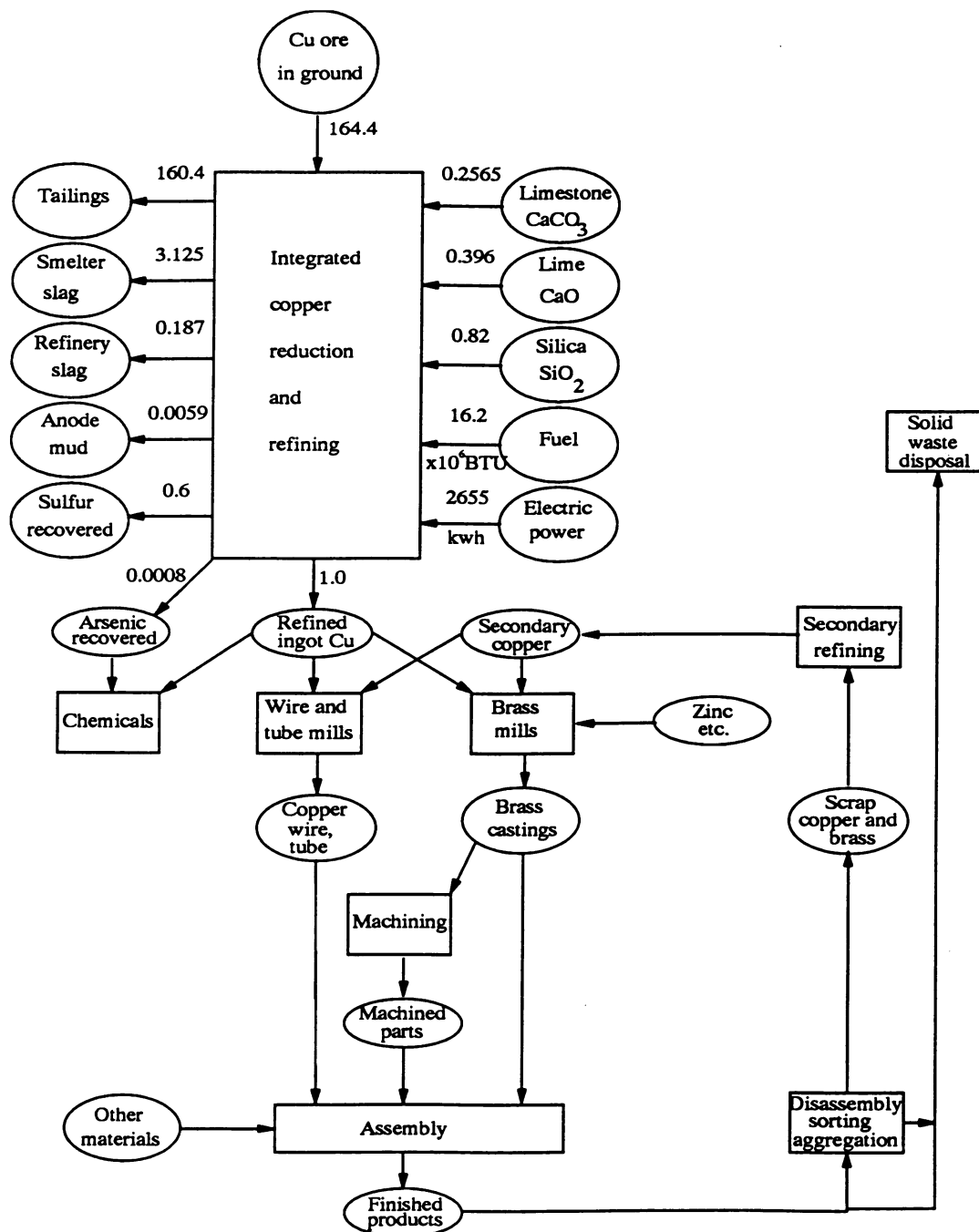


FIG. 3. Copper cycle. All numbers indicate units per unit of refined copper output. BTU, British thermal units; kwh, kilowatt hours. Data are from Argonne National Laboratory (Argonne, IL).

chemicals are somewhat toxic. The dominant use of silver in recent decades has been as the light-sensitive element in photographic films. There is some recycling from film processing laboratories, but as photographs and negatives are dispersed, so is silver. Eventually old photographic materials end up in landfills or fires. A severance tax to increase the price of virgin silver would improve the economics of recycling significantly in the short run. Eventually, dissipative uses could probably be eliminated. Advances in photochemistry have decreased the amount of silver needed for this purpose more rapidly than the dissipative uses have grown in recent years.

In principle, there could be a significant accumulation of toxic materials in the anthroposphere (the accumulation of permanent structures, long-lived durable goods, and permanent forms of waste storage), provided these materials are not dissipated into the other spheres at unacceptable rates. Thus, all except the most benign materials, once extracted from the earth, must be contained more or less permanently within the anthroposphere. This requirement obviously applies particularly to nuclear materials and toxic heavy metals. In effect, it is necessary for long-run human survival to create closed cycles within the anthroposphere for all such materials. Such closed cycles, in turn, will require the creation of a number of new chemical and metallurgical process technologies.

For example, although lead-based automotive batteries are already 90% recycled within 5 years, several firms are developing improved processes for this purpose. One is the Italian Ginatta process, where the spent batteries have their bottoms cut off and are immersed directly in an electrolyte. Several companies are developing processes for recovering lead from battery sludge.

To take another example, the Bureau of Mines is working on a process to recover precious metals (mainly silver and gold) from discarded mixed electronic devices. The process involves shredding, air classification, wire picking, magnetic separation and sizing, and eddy current separation. Obviously, a process as complex as this can only be justified if the supply of scrap is continuous and large, and if the value of the recovered materials is fairly high. On the other hand, once the basic technology is developed, there is no reason it should not be extended to permit the recovery of copper, rare earths, semiconductors, and so on.

It seems clear that technological fixes alone will not close the materials cycle for these metals. Many dissipative uses will eventually have to be banned. Severance taxes (supplemented by import taxes) on the major nonferrous metals should be effective in reducing the supply of by-products. Refundable deposits would probably be effective in increasing the recycling of cadmium and mercury batteries. Even more drastic measures, such as "no discharge" rules and mandatory trade-ins, might also be required in the long run.

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