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Lead in South Africa

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SYNOPSIS

This paper reviews lead as a commodity, starting with a brief historical outline and dealing with the various uses of lead in some detail. It then goes on to discuss some statistics in relation to the production and reserves of lead, before sketching its mode of occurrence. The topics are approached in regard both to the world and to South Africa, with the emphasis on the latter.

The mining and concentration of lead at Black Mountain Mine at Aggeneys in the north-western Cape Province are detailed, before a general account is given of the smelting, hydrometallurgical extraction, and refining of lead, together with the processes used in these activities.

The paper concludes with a discussion of safety and health in regard to lead and a brief look at the commodity's future.

SAMEVATTING

Hierdie referaat gee 'n oorsig oor lood as 'n kommoditeit deur te begin met 'n kort geskiedenis in hooftrekke en daarna die verskillende gebruike van lood in besonderhede te bespreek. Dit gaan dan verder en bespreek statistiek wat betref loodproduksie en -reserwes voordat dit die voorkomswyse skets. Die onderwerpe word met betrekking tot sowel die wêreld as Suid-Afrika benader, met die klem op laasgenoemde.

Die ontginning en konsentrasie van lood by die Black Mountainmyn by Aggeneys in Noordwes-Kaapland word in besonderhede bespreek voordat daar in die algemeen verslag gedoen word oor die uitsmelting, hidrometallurgiese ekstraksie en raffinering van lood, asook die prosesse wat vir hierdie werksaamhede gebruik word.

Die referaat sluit af met 'n bespreking van veiligheid en gesondheid met betrekking tot lood, en 'n kort kykie op die toekoms van die kommoditeit.

Introduction

Of the elements in the earth's crust, lead ranks 34th in abundance and is one of the most widely used metals in the industrial world. The useful characteristics of lead are unrivalled and at present it has no substitute in most of its uses. Its unique properties include high density, high ductility and malleability, low creep resistance and softness, low melting point, high resistance to chemical attack and corrosion, easy shaping and castability, and sound-wave and X-ray attenuation.

Lead is one of the oldest metals used by man and, even today, one of the most useful and essential[1]. Its use dates back to between 5000 and 7000 B.C., when the early Egyptians used it for glazing pottery. The first known specimen of lead, dating from before 3800 B.C., is in the form of a figure found at the Dardanelles on the site of an ancient city called Abydos. The earliest known mines were established by the Phoenicians, who mined lead in Spain, Greece, Sardinia, and Cyprus, to be followed by the Romans who had lead mines in Spain, England, Gaul, and the Eifel Mountains. In the Middle Ages, deposits were developed in Germany at Rammelsberg and in the Erzgebirge.

Although there was a lead production boom in Europe during the 16th century, larger deposits were developed in the 19th and, principally, the 20th centuries in the U.S.A., Mexico, Canada, Australia, and South Africa.

In South Africa[2] lead was first discovered at the Maitland River in 1782 and was worked for a short period early in the 19th century. Before the introduction of breech-loading arms, lead was smelted in the Transvaal for use in the Boer Republics. The lead deposits that were exploited were mainly in the Transvaal near Argent[3] station, where a smelter was erected between 1889 and 1893. Between 1922 and 1925, the Argent Mines and Smelter were operated by Transvaal Silver & Base Metals Limited, which produced about 360 t of crude lead per month from a blast furnace for refining overseas.

These Argent deposits were mined intermittently until 1957, when they finally closed down, the most productive periods being between 1882 and 1893, 1922 and 1925, and 1951 and 1957. A total of 16 250 t of metallic lead was produced. Other deposits mined during those periods were in the Marico district, at Edendale near Pretoria, and at the Ballock Mine in the Cape Province.

Uses of Lead

Many of the historical uses of lead continue to remain important reasons for its present demand. Such uses include glazing for pottery, castings, sheet, solder, pipes, coinage, and bronze. Major 'new' uses include storage batteries, gasoline additives, cable sheathing, paint pigments, and protection against radiation in the nuclear field. About 60 per cent of the lead produced is consumed in metallic form, while 40 per cent is converted to lead compounds.

The consumption of lead can be divided into two categories: dissipative and non-dissipative. The first precludes the recovery or recycling of any lead, and refers to such uses as gasoline additives or paint pigments. Non-dissipative consumption is mainly in the battery sector, where the bulk of the metal can be recycled.

The major uses of lead in the world in 1981 are shown

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TABLE I
WORLD USES OF LEAD[4] (1981)

Uses	Consumption kg	Percentage of total
Batteries	1711	51
Pigments	472	14
Rolled and extruded	287	8
Cables	257	8
Gasoline additives	209	6
Alloys	167	5
Miscellaneous	161	5
Shot/ammunition	88	3
Total	3352	100

in Table I. By far the largest single use for lead is in car batteries, which consume about half of the world's annual production.

The use of lead as a gasoline additive has come under increasing pressure, and it is being phased out in most industrial countries. Tetraethyl lead is added to gasoline as the most convenient and economic way of producing the high octane grades that are needed for the efficient operation of engines of high compression ratio. By its use, the costs of oil refining are reduced, energy is saved, and more high-grade fuel is obtained from a given quantity of crude oil.

Although the lead industry is regarded as a hazard to the environment, lead plays an important role in the protection of the environment (including the work environment). Good examples are the electric cars and electric locomotives used in mines, which are powered by lead-acid batteries.

Lead is also used in cable as a sheathing material for protection against corrosion and mechanical stresses. Lead pipes are used in numerous household and chemical applications, and it is interesting that lead pipes in almost perfect states of preservation have been dug up in recent years in the ruins of Pompeii and Rome. Substitution by aluminium and plastics has reduced the demand in these sectors and is expected to continue to do so in the future.

The major outlets for lead alloys are solders, bearings, and printing metal, the main users of solder being the automobile, canning, and electrical industries.

Table II gives the major uses of lead in South Africa in 1982.

TABLE II
CONSUMPTION OF LEAD IN SOUTH AFRICA[5] (1982)

Uses	Consumption kg	Percentage of total
Batteries	27,7	53,2
Cable sheathing	10,6	20,3
Chemicals	6,5	12,5
Wire rope	1,6	3,1
Lead sheet	2,5	4,8
Solder	1,0	1,9
Ammunition	1,2	2,3
Other	1,0	1,9
Total	52,1	100,0

In South Africa, as in the rest of the world, batteries account for about half the consumption. The battery market is structured roughly as follows:

		Per cent
Automobile—	Replacement	48
	New equipment	24
	Total	72
Electric vehicles		17
Standby power		11
		100

A wide range of chemicals are produced from lead in South Africa for a variety of uses. Some examples are given in Table III. Other lead-containing materials produced in South Africa are solder, bearing metals, lead foil, printers metal, and ammunition.

TABLE III
USES OF LEAD CHEMICALS PRODUCED IN SOUTH AFRICA

Material	Use
Pigment/Compound	
Assay litharge	Analysis for precious metals
Calcined litharge	Glass Paint Batteries
Red lead (Pb_3O_4)	Paint
Lead sulphate	Brake linings
White lead	Paint Metal pressing
Lead nitrate	Gold recovery
Stabilizer/Lubricant	
Dibasic lead phthalate	Used mainly for plastics and rubber
Dibasic lead phosphite	
Dibasic lead stearate	
Lead salicylate	
Tribasic lead maleate	

World Production of Lead

Lead is produced from two main sources: primary lead from ore by smelting and refining, and secondary lead from refining scrap. Both methods result in lead of very high purity.

Lead is mined in 50 countries of the world in over 400 mines, which accounted for the 1984 production of 3,25 Mt of lead in concentrates[6]. South Africa's contribution amounted to 2,9 per cent of this production. Most industrial countries, such as Belgium, France, Germany, England, and Japan, are deficient in mineable reserves to meet smelter requirements and most of them import concentrates.

In 1983 the production of refined lead in the Free World was as follows[7,8]:

Source	*Production, Mt*
Primary production	2,35
Secondary production	1,58
Total	3,93

In South Africa the only lead metal produced is from secondary production, all the concentrates (from primary production) being exported for further treatment. Countries purchasing South African lead concentrates include Canada, Germany, Australia, and France.

Primary Lead Production in South Africa

The production of lead concentrate in South Africa is shown in Table IV. It can be seen that from 1957, when the Argent smelter finally closed down, production was erratic and almost insignificant until 1980, when the Black Mountain Mineral Development Company began producing. In that year South Africa became a net exporter of lead for the first time.

TABLE IV
LEAD PRODUCTION IN SOUTH AFRICA[9]

Year	Production, t
1957	1 665
1958	64
1959	209
1960	169
1961	133
1962–63	32
1964	–
1965	64
1966	–
1967	27
1968–71	–
1972	182
1973	2 164
1974	3 008
1975	3 605
1976–79	–
1980	86 059
1981	98 901
1982	90 288
1983	87 533
1984	94 764

Black Mountain Mineral Development Company (Pty) Limited (Fig. 1) has an annual production of 1,1 Mt of ore containing lead, copper, zinc, and silver. The mine is situated at Aggeneys in the north-western Cape Province, and production is from the Broken Hill orebody. The annual production of concentrate is lead 130 kt, copper 20 kt, and zinc 48 kt. Silver reports with the lead and copper concentrates. The following is a typical analysis of the lead concentrate:

Pb	70%
Cu	0,5%
Zn	2,5%
Ag	750 g/t.

Shell South Africa is developing a new zinc–lead mine at Pering, 75 km from Vryburg in the northern Cape Province. Production is scheduled to start towards the end of 1986. Although the mine will be mainly a zinc producer, it is estimated that the annual lead production will be between 10 and 15 kt of concentrate at a lead grade of 60 per cent.

At present there are two producers of secondary lead in South Africa but, owing to the intense competition in the market, it is difficult to obtain any reliable statistics. The capacities of the secondary smelters are as follows:

	Capacity, kt/a
Castle Lead Works	3
Frys' Metals:	
Germiston plant	20
Port Elizabeth plant	8
Total	31

The production of secondary lead is limited by the availability of scrap, which is derived mostly from scrap batteries (Table V). Other sources are cable sheathing, lead pipe and fabricator drosses, slags, and residues. Battery scrap was imported in the past, but this has become prohibitively expensive, and it is suspected that importation no longer takes place.

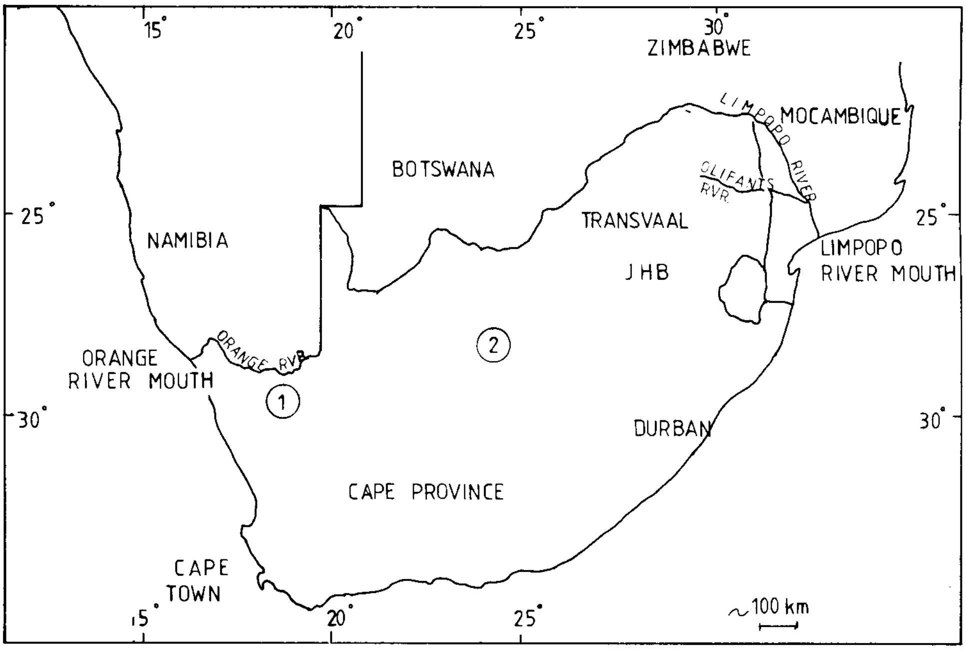

Fig. 1—Lead operations in South Africa
1. **Black Mountain Mineral Development**
2. **Pering (Shell S.A.)**

TABLE V

SOURCES OF LEAD SCRAP[5] (1982) (IN TONS)

Source	Transvaal and O.F.S.*	Natal	Cape	Total
Car batteries	6 600	1 500	2 600	10 700
Other batteries	4 500	750	750	6 000
Other scrap	1 500	750	750	3 000
Local scrap	12 600	3 000	4 100	19 700
Imported scrap				11 400
Total				31 100

*Orange Free State

Lead Reserves

In a consideration of lead resources, a differential must be made between total resources and reserves. A resource constitutes a reserve when it can be exploited economically and its size, grade, and nature are known in detail.

The world reserves of lead have been estimated as shown in Table VI.

TABLE VI

WORLD RESERVES OF LEAD[6]

Country	Reserve base × 1000
U.S.A.	27 000
Australia	28 000
Canada	17 000
Mexico	4 000
Morocco	2 000
Peru	3 000
Republic of South Africa	5 000
Yugoslavia	5 000
Other market-economy countries	16 000
Centrally planned economies	28 000
	135 000

The identified sub-economic lead deposits in the world have been estimated at $1,4 \times 10^9$ tons. These deposits require new technology for development and recovery, and the probability of finding additional economic resources is considered highly favourable.

The South African reserves of lead are shown in Table VII.

TABLE VII

SOUTH AFRICAN LEAD RESERVES[10]

Deposit	Ore Mt	Lead content %	Metal content Mt
Broken Hill	21,5	8,35	1,795
Black Mountain	41,0	4,19	1,718
Big Syncline	100,0	1,01	1,010
Gamsberg	143,0	0,50	0,715
Pering	17,4	0,66	0,115

South African Lead Requirements

South Africa requires between 50 and 55 kt of lead per annum. This demand was met from the following sources in 1982:

Secondary lead	26 824 t
Imports: Tsumeb	20 900 t
Zambia	3 976 t.

As can be seen from these figures, only half the demand was met by local production (from secondary producers). Zambia will probably cease to be a source of lead since its production is expected to end within the next five years.

Mode of Occurrence of Lead[11]

Geology

Lead deposits can be divided into five broad geological categories.

Stratabound sedimentary deposits are commonly found in limestones or dolomites and are the most productive source of lead. The best examples are found in the Missouri lead belt.

Volcanic sedimentary deposits include massive sulphide bodies interlayered with volcanic and sedimentary rocks.

Replacement deposits are generally irregular hydrothermal deposits in carbonate, quartzite, or metamorphic rocks.

Vein deposits are the most obvious of the lead deposits and the first to be exploited. However, they are of minor commercial importance.

Contact metamorphic deposits are found near igneous intrusions, which have either provided the mineral-rich solutions or have altered a mineral-rich rock to form the deposit.

Mineralogy

More than 130 lead minerals occur in nature, galena (PbS) being of the greatest economic importance. The near-surface parts of some of the lead orebodies have galena altered to cerussite ($PbCO_3$) or anglesite ($PbSO_4$), and these minerals are also exploited. However, 90 per cent of the world's lead is extracted from galena.

Deposits of lead ore are usually complex, the most common associated sulphide minerals being pyrite (FeS_2), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), tetrahedrite ($3Cu_2S.Sb_2S_3$), argentite (Ag_2S), and other sulpho salts. Sphalerite, in particular, is nearly always associated with galena, and it is rare to find one of these minerals without the other.

In virtually all the mines in the world producing lead today, zinc, and to a lesser extent silver and copper, are also produced, Galena almost always has a silver content of between 0,01 and 0,03 per cent. Other elements invariably associated with lead are bismuth, arsenic, and antimony.

In South Africa

More than 50 occurrences of lead have been reported in South Africa[2], but these are mainly small and economically insignificant. The deposits occur almost exclusively in quartz veins or in dolomite. The most significant occurrence is on the farm Aggeneys in Namaqualand, where the Black Mountain Mine has been established.

The ore deposit at Aggeneys[12,13] consists of three complex orebodies: Broken Hill, Black Mountain, and Big Syncline. Exploration started in 1929 but it was only after 1971, when Phelps Dodge conducted an extensive diamond-drilling programme, that the potential of the deposits became clear. The ore reserves and grades are shown in Table VII. The present mining operations are based on the Broken Hill deposit, which consists of two distinct orebodies—the upper and lower lenses. The orebodies extend over a strike length of 1600 m from a surface outcrop in the west to about 800 m in the east. They run conformably and are separated by an intermediate schist. The dip is to the north at 55 degrees near surface, and varies from almost flat to 40 degrees in the lower western portion of the orebodies.

The stratigraphy (Fig. 2) consists primarily of footwall schists, which contain little or no water. A weak zone 3 m thick, consisting of graphite and mica-rich ground, occurs in the footwall. It is unconsolidated and presents problems of strata control when exposed.

The orebodies consist essentially of high-grade massive sulphide lenses situated on a geological footwall, with low-grade magnetites in the hangingwall. The orebodies and the hangingwall quartzites contain water, which is associated with fissures and cracks. The massive sulphide contains abundant galena and pyrrhotite, with lesser amounts of sphalerite, chalcopyrite, and pyrite. Galena is the dominant economic constituent of the amphibole magnetite, with associated sphalerite and chalcopyrite. Pyrrhotite is the dominant iron sulphide. The massive sulphide varies from 5 to 55 per cent lead, with isolated zinc contents as high as 20 per cent. The lead content of the amphibole magnetite varies from 0,3 to 5 per cent.

Mining at Black Mountain

Except for a few large surface-mining operations in Canada, almost all the world's lead ores are produced from underground mines. This is normally because the depth and nature of the orebodies does not permit open-pit extraction, although the economics must be examined in each case. The method of underground mining is determined by the nature and dip of the orebody.

At Aggeneys[14,15], because of the high grade of the Broken Hill orebody, it was considered of prime importance that the mining method used should permit maximum extraction of the orebody. Access to the orebody is via a 11-degree spiral decline 1800 m long and a 5,5 m by 4,4 m three-compartment vertical shaft. Two mining methods were selected: blasthole stoping and cut-and-fill mining.

Blasthole stopes were developed in the upper areas, where the orebody dipped at more than 50 degrees. This is a mass mining method and high production rates were achieved. The blasthole stoping area is divided into primary stopes and pillar reclamation. As the primary stopes are extracted, they must be filled so that the adjacent pillars can be extracted. The primary stopes were backfilled with a mixture of sand, tailings, and cement, and the pillar stopes only with sand.

In general, the grade decreases with distance from the blasthole stoping area. As the flatter dip of the orebody in the lower regions excluded blasthole stoping, cut-and-fill mining was selected. Basically, the method implies that the orebody is mined out by the cutting of horizontal slices 4 m thick for a distance of 200 m on the strike of the orebody. The open void is then filled to within 1 m

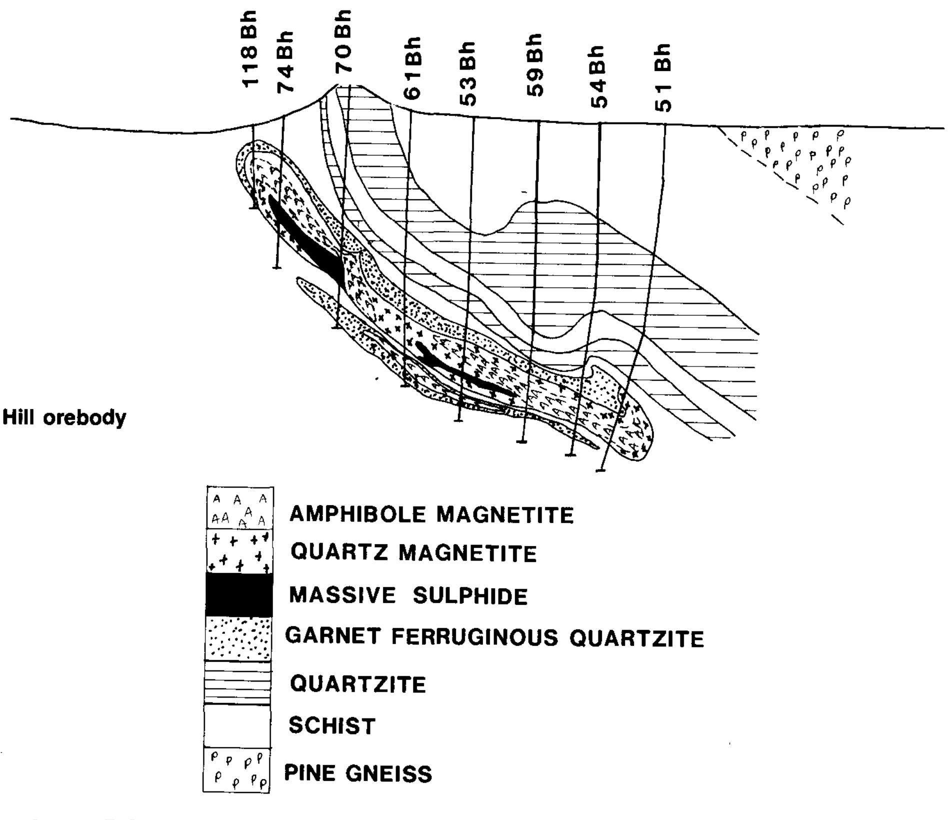

Fig. 2—Section through the Broken Hill orebody

of the reef, and the sequence is repeated, with the stope progressing up-dip. The cut-and-fill mining at Black Mountain is highly mechanized. Tamrock Paramatic two-boom rigs and pneumatic or hydraulic drifters are used to drill horizontal 51 mm diameter holes for rock breaking. Cleaning is done by means of Wagner S.T8LHD units. Both of these units are rubber-tyred, and the quality of the fill must permit access by either machine within 24 hours.

The main reason for the selection of cut-and-fill mining was that it allows for 100 per cent extraction of the orebody. Unlike the footwall contact of the orebody, the hangingwall has an economic cut-off, which is based on the combined economic value of the constituent metals. The stoping method is flexible since, once a face has been established, it can follow the convolutions of the orebody according to geological or economic dictates.

The backfilling technique (Fig. 3) employs a 2,25 m base layer of sand, capped with a 0,75 m layer of classified mill tailings and Portland cement in the ratio 10:1. During mining operations, up to 2 per cent by mass of the capping can be removed as dilution into the ore, which creates some metallurgical problems in the concentration process.

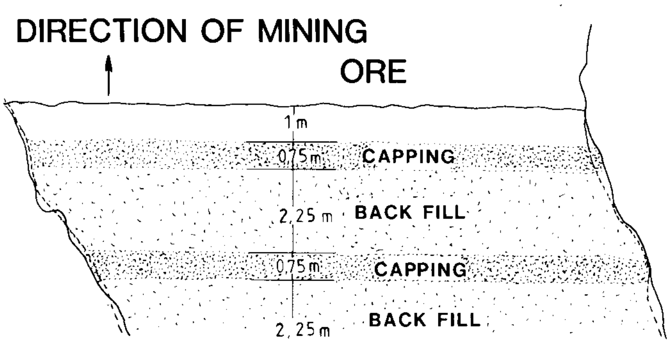

Fig. 3—Backfilling cut-and-fill stopes

Blasted ore is fed into two 1300 t ore silos on 10 level, and from there is crushed to minus 150 mm in a Hadfield jaw-crusher below 11 level. The crushed ore is conveyed to five 700 t storage silos, from which it is hoisted to surface.

Concentration at Black Mountain[16]

As few lead ores in the world are sufficiently rich in lead and low in impurities to be smelted directly, most lead ores must be upgraded to a suitable concentrate. The usual procedure in this upgrading involves the crushing and grinding of the ore minerals in order to liberate them from waste material and other minerals in the ore. Lead ores of simple composition such as disseminated-lead or lead–zinc ores are concentrated by heavy-medium separators, jigs, or tables.

Unlike the lead ores of the Mississipi Valley, which are of this simple type, the Broken Hill ores are complex, the economic minerals being disseminated in two distinctly different ore types: massive sulphide with a Bond work index of 12 kW/t, and magnetite amphibole with a Bond work index of 18 kWh/t. Owing to the complex nature of the ore, the economic minerals can be separated by flotation only after fine grinding.

Crushing

After primary crushing underground to minus 150 mm, the ore is hoisted to surface, where it is stored in five coarse-ore silos each with a nominal capacity of 1200 t.

The fine-crushing circuit consists of one secondary and two tertiary Allis Chalmers Hydrocone crushers of 1,5 m diameter, with associated screens. The crushing plant operates 2 shifts a day for 6 days a week. The product from tertiary crushing at minus 16 mm is stored in five fine-ore silos with a capacity of 1200 t each.

Milling

The milling section consists of a 3,2 m by 4,9 m rod mill in open circuit, and a 4,9 m by 5,25 m ball mill operating in closed circuit with a cluster of five cyclones each of 505 mm diameter.

The ore in the milling circuit is alkaline owing to contamination by cemented backfill. Zinc sulphate and isopropyl ethylthionocarbamate (Z200) are fed to the rod mill, the former to depress the zinc and the latter to collect the copper.

Flotation

Copper, lead, and zinc are generally recovered from complex sulphide ores by bulk flotation followed by separation of the copper lead and zinc sulphides, or by sequential differential flotation. The latter is the method employed at Black Mountain, the order of the sequential flotation being copper sulphide, lead sulphide, zinc sulphide. The copper-flotation circuit is beyond the scope of this paper and has been described elsewhere[19,20]. The lead-flotation circuit is shown in Fig. 4.

The density of the tailing from the copper circuit is adjusted in a thickener to 1,7 prior to its introduction to the lead circuit. The pulp is conditioned in four conditioners before flotation. The pH value is adjusted to 8,5 in the first conditioner with lime or soda ash, the latter being preferred. Calcium cyanide and zinc sulphate are added to the second conditioner to depress the sulphides of iron and zinc, and two collectors are added to the third conditioner: Cyanamid R242 (aryl dithiophosphoric acid) and sodium ethyl xanthate. MIBC is added as a frother.

Rougher flotation takes place in two parallel banks of 9 Outokumpu cells with a volume of 8 m^3 each. Rougher concentrate is cleaned in three stages in two rows of 15 Outokumpu 3 m^3 cells. Rougher scavenger tailings proceed to zinc sulphide flotation while the final concentrate is pumped to a Dorr Oliver thickener of 20 m diameter. The lead-concentrate thickener underflow is filtered until its moisture content is about 7 per cent before being despatched by truck to Loop 10 and from there by train to Saldanha Bay. To achieve the required moisture content, filter aid is added and, when necessary, the pulp is heated with steam.

Lead Smelting

More than 90 per cent of the world's primary lead production is from classical lead smelters using the roast–reduction process in sinter machines and blast furnaces. About 7 per cent of the total production emanates from the Imperial Smelting Process, which is similar to lead blast-furnace technology. The remaining 3 per cent is produced by electrothermal and rotary-hearth processes.

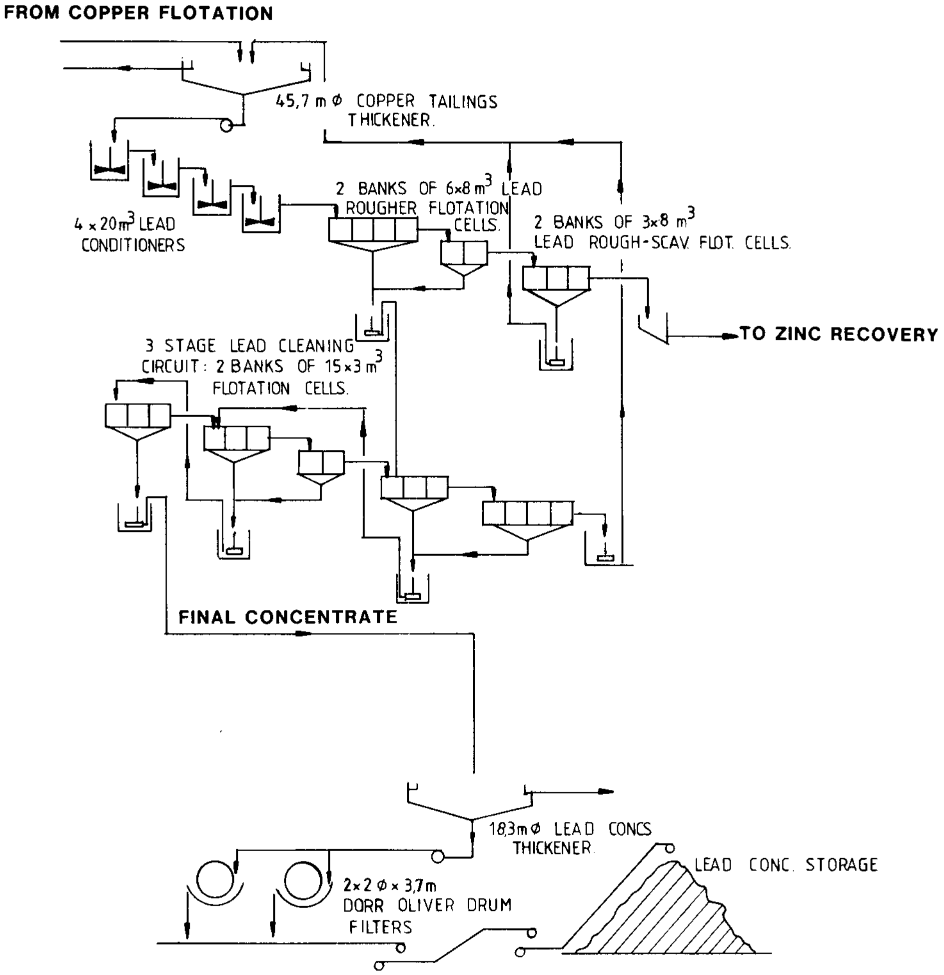

Fig. 4—The lead-flotation circuit at Black Mountain

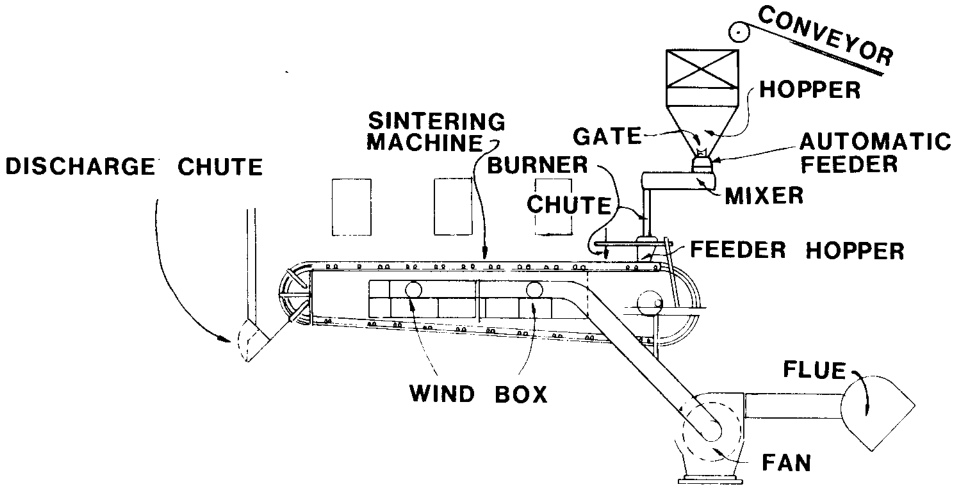

Fig. 5—Sintering machine used in conventional lead smelting

Conventional Process

In the conventional smelting process, which has been in operation for over a century, lead concentrate is mixed with fluxes and recycle products, and is then desulphurized and agglomerated on a sinter machine. The sintering machine (Fig. 5) is basically a moving grate through which combustion air is passed. Off-gases are removed from the grate and treated further for the recovery of dust, and sometimes sulphuric acid. (The sulphur dioxide content is often very low.)

The sinter clinker, which must be firm and porous, is broken into lumps of up to 150 mm in size and the fines removed by screening are recycled.

A lead blast furnace (Fig. 6) consists mainly of a water-jacketed shaft that is charged at the top. The shaft is supported by a heavy refractory base, which forms the crucible and lead well.

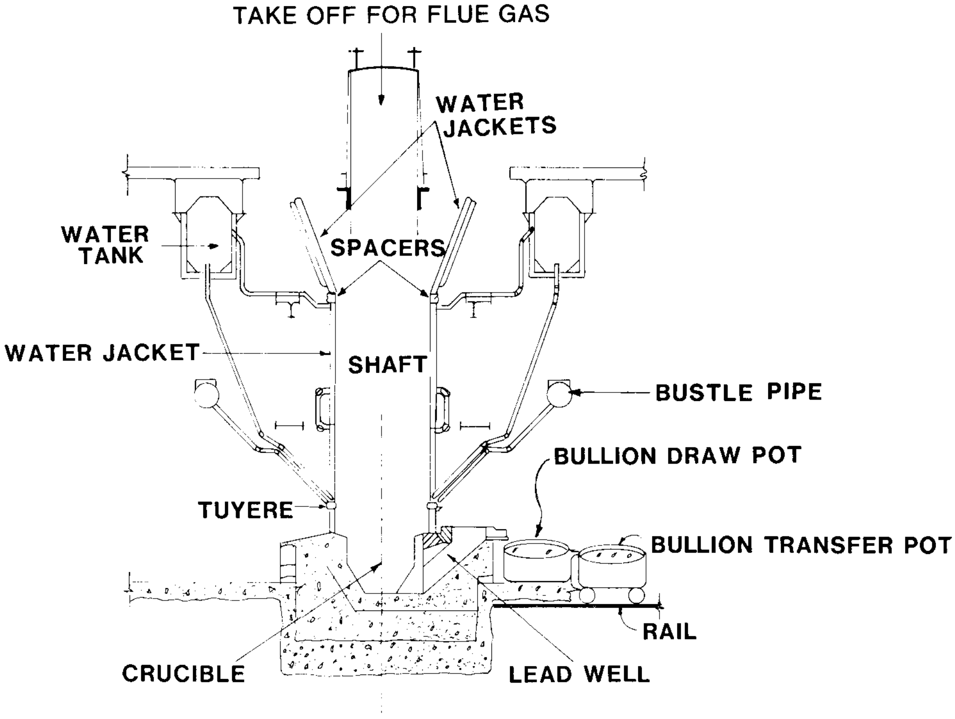

Fig. 6—Cross-section through a lead blast furnace

The process is shown in Fig. 7. Roasted sinter is mixed with limestone flux, and about 14 per cent coke and blast air are introduced through tuyères in the lower part of the furnace. A temperature of about 1400°C is produced by the burning of coke to form carbon monoxide and dioxide. Oxidized lead compounds are reduced by the carbon monoxide and hot coke to bullion (94 to 98 per cent lead), which is tapped continuously from the lead well. Copper, iron, cobalt, and nickel present in the feed combine with the sulphur in the charge to form a matte that can be tapped from the front of the furnace. Zinc present in the ore accumulates in the slag, while precious metals are removed with the bullion for separation in subsequent refining operations.

The lead recovery from the concentrate is normally between 97 and 99 per cent. Lead bullion contains metals such as gold, silver, antimony, arsenic, copper, tin, and zinc, which are removed by further refining.

The process is expensive and inefficient in relation to its energy utilization, and circulating loads of up to 80 per cent of the sinter are encountered in practice. The sulphur dioxide content of the off-gases is very low, making the production of byproduct sulphuric acid difficult. Pollution of the working environment with metal vapours and sulphur dioxide is difficult to control, and the new standards for work-place hygiene can be met only by vast capital expenditure, if at all.

These factors have resulted in a concentrated effort over a number of years to develop more suitable technologies for the smelting of lead.

New Developments in Lead Smelting

The combination of increasingly restrictive environmental and workplace exposure laws, along with the high operating costs associated with the conventional sintering and blast-furnace technology, have provided compelling reasons for the development of new lead-smelting processes[19,20].

This development began in the mid 1960s, and all the alternative processes involve the direct smelting of lead sulphide in a single step according to the partial oxidation reactions

$$PbS + O_2 \rightarrow Pb + SO_2$$
$$PbS + PbSO_4 \rightarrow 2\ Pb + 2\ SO_2.$$

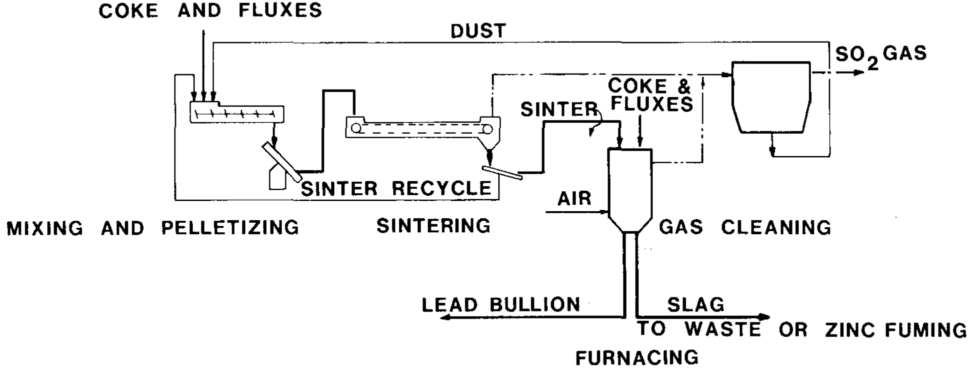

Fig. 7—Lead-sintering and blast furnace process

Another aspect common to the new technologies is that the volume of smelter off-gas is much less, and they all claim to meet strict environmental-pollution regulations.

The direct smelting technologies that are considered to be the most advanced to date are the Outokumpu, Kivcet, and Boliden Kaldo flash-smelting processes and the Lurgi Q.S.L. process. None of these processes is yet in commercial operation, but the development has proceeded to pilot-plant level.

Outokumpu Flash Smelting

This process[21], which is illustrated in Fig. 8, is based on the copper flash smelter and was developed for lead in 1964. Dried lead concentrate mixed with limestone and silica flux is fed to the reaction shaft of the flash smelter with oxygen-enriched air. Smelting is usually autogenous but in some cases extraneous fuel is required.

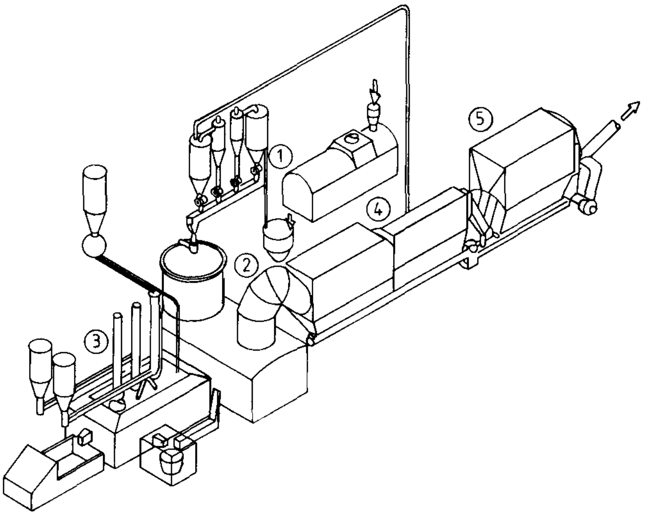

Fig. 8—Outokumpu process
1. **Dryer**
2. **Outokumpu flash-smelting furnace**
3. **Slag-cleaning furnace**
4. **Gas cooler**
5. **Electrostatic precipitator**

The furnace products are lead bullion, sulphur dioxide, and slag still rich in lead. The direct recovery of lead in the furnace can be up to 95 per cent but depends on the quality of the concentrate and the degree of oxidation. The higher the degree of oxidation, the less bullion is produced, the lower the sulphur content of the bullion, and the higher the lead content of the slag. Slag from the furnace is tapped continuously into an electric furnace, where the contained lead is recovered by the injection of coal dust.

Kivcet Flash Smelting

The Kivcet process[22] (Fig. 9) was developed in the U.S.S.R. and is very similar to the Outokumpu process. The main difference is that Kivcet combines smelting and reduction in a single unit (although in separate but connected compartments). A commercial-scale plant has been built in Bolivia but has not been commissioned. The problems have been mainly of a political nature, and feed for the plant was not readily available.

Boliden Kaldo Flash Smelting

A top-blown rotary converter is used in this process[25,26] (Fig. 10), and the oxidation and reduction steps are done in the same vessel. A mixture of dried concentrate and fluxes is introduced into the vessel through a lance with oxygen-enriched air. Smelting takes place in flight, and the reaction is autogenous.

The product of this first-stage smelt is a rich sulphur dioxide gas, lead bullion high in sulphur, and a lead-rich slag. In the reduction stage that follows, the lead in the slag is reduced by the introduction of coke through a separate lance. The sulphur content of the bullion is reduced by the reaction

$$2\ \mathrm{PbO} + \mathrm{PbS} \rightarrow 3\ \mathrm{Pb} + \mathrm{SO_2}.$$

The furnace is totally enclosed, which permits efficient environmental control.

Ventilation gases are cleaned separately from process gases in a bag filter. The main disadvantage of the process is that its production of sulphur dioxide gas is intermittent (because the process is batch operated).

Q.S.L. Process

The Q.S.L. process[27,28] (Fig. 11) named after its inventors, Professors P. Queneau and R. Schuhman, and its developer, Lurgi, has been the subject of an ongoing development programme since 1974. It is a continuous direct lead-smelting process. The technology incorporates two basically different pyrometallurgical operations in a single vessel: an autogenous-roast reaction smelting of galena, followed by carbothermic reduction of lead oxide slag.

The charge is smelted continuously in a long horizontal cylinder, which is lined with bricks of fused chromium–magnesite. Green pellets, consisting of galena concentrate and a flux, are dropped into the oxidation zone and dissolve in the molten bath. Oxygen is injected into the bottom of the bath at one end to form lead bullion, sulphur dioxide, and a lead oxide slag. The slag runs continuously to the reduction zone of the reactor, where its contained lead is reduced by the submerged injection of pulverized coal. The reduced slag is tapped continuously from the vessel, and the bullion recovered from the slag moves countercurrently to join the primary produced bullion. The bullion is tapped continuously at the flue end of the reactor. The whole reactor is under a slight negative pressure, and the in-plant hygiene standards and work environment can be controlled effectively.

Extensive development and tests have been conducted in a 25 kt/a demonstration plant at Berzeluis in Duisberg, West Germany. The latest modification to the reactor is a low partition of refractory to separate the two zones and to prevent backmixing of slag. The partition has an opening at the bottom for the passage of slag. By January 1984, more than 40 kt of lead-bearing material had been treated in the demonstration plant, which is to be dismantled in 1986.

Lead Smelting in South Africa

At present there is no facility for primary lead smelting in South Africa, although the need for such a facility was recognized a number of years ago. The main reason attributed to this situation is that economics favour the sale

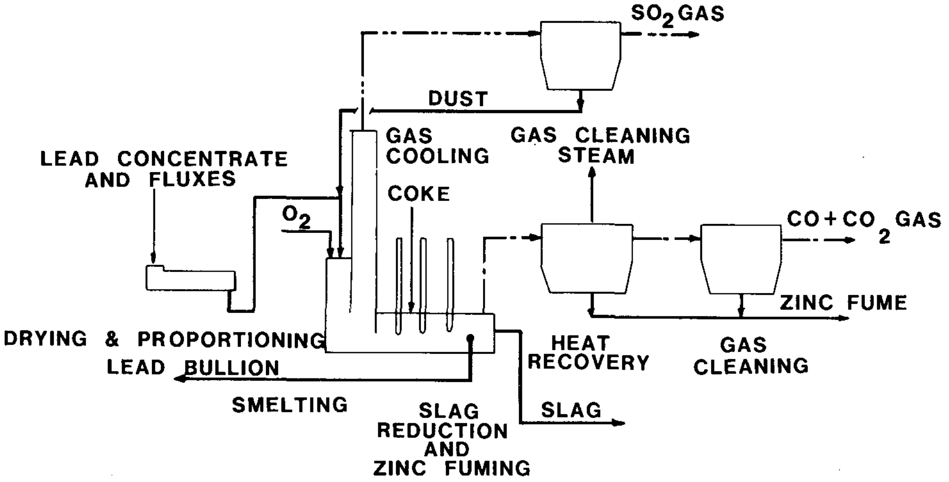

Fig. 9—Kivcet lead-smelting process

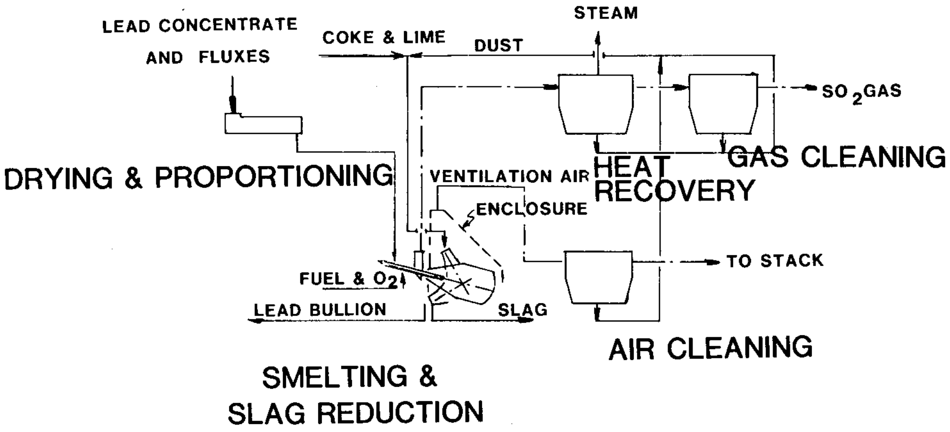

Fig. 10—Boliden Kaldo lead-smelting process

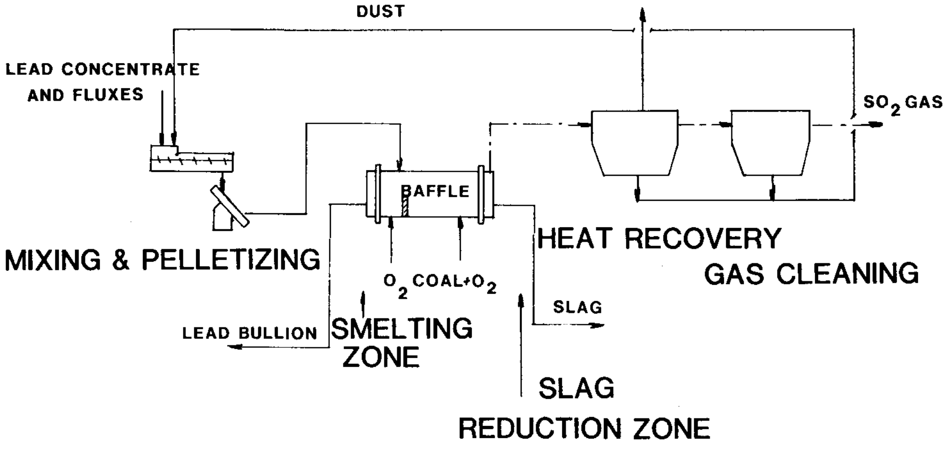

Fig. 11—Q.S.L. lead-smelting process

of concentrates in spite of a premium of approximately R80 per ton on local lead prices.

As mentioned previously, the only production of lead metal in South Africa is from secondary sources. The secondary production of lead can be described as melting rather than smelting, since the recycle material consists mainly of old batteries.

Hydrometallurgical Extraction of Lead

In parallel with pyrometallurgists investigating direct-smelting options, hydrometallurgists have studied chloride-based leach–electrolysis processes for the recovery of lead from galena. Although hydrometallurgical processes largely avoid the pollution problems resulting from metal fumes and sulphur dioxide, a new potential source of pollution (from heavy-metal chlorides in the leach residues) is introduced.

A major advantage of the chloride leaching route is considered to be the formation of elemental sulphur:

$$PbS + 2\,FeCl_3 \rightarrow PbCl_2 + 2\,FeCl_2 + S.$$

The two hydrometallurgical routes for lead extraction that are considered to be the most advanced are those developed by Minemet Recherche in France and the U.S. Bureau of Mines in the U.S.A. (Reno). Both processes have been operated extensively on pilot-plant scale.

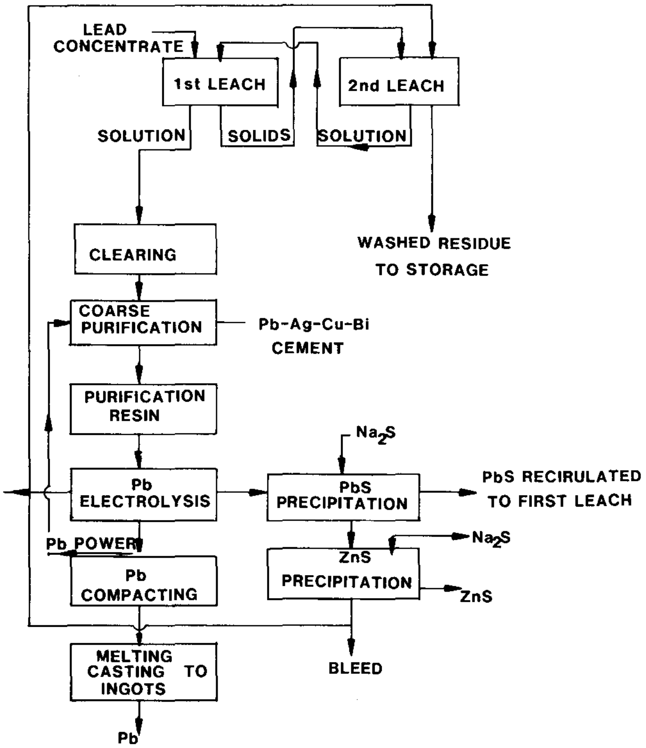

Fig. 12—Minemet lead process

Minemet Process

In the Minemet process[27] (Fig. 12), galena concentrate is reacted in a two-stage countercurrent leach with a medium of sodium and ferric chlorides. The temperature of the leach is maintained at 90°C with a high concentration of ferric ions in the second stage and a low concentration of ferric ions in the first stage. Other metals besides lead that are attacked by the leaching medium are typically copper, zinc, silver, bismuth, and cadmium. The insoluble residue consists essentially of pyrite, elemental sulphur, and silica.

The pregnant liquor is clarified, and coarse purification takes place by the addition of lead powder. The metals cemented out include bismuth, copper, and silver via reactions similar to

$$2\,AgCl + Pb \rightarrow PbCl_2 + 2\,Ag.$$

In order to produce lead with a purity of 99,99 per cent, a further purification step is required. An ion-exchange resin is used to provide the final purified solution, which is sent direct to an aqueous electrolysis cell of the membrane type. The main cell reactions are as follows:

$$\text{Cathode:}\quad Pb^{2+} + 2\,e \rightarrow Pb$$
$$\text{Anode:}\quad 2\,Fe^{2+} - 2\,e \rightarrow 2\,Fe^{3+} + 2e.$$

Lead powder is removed from the cathode, compacted, and melted. A bleed stream is taken from the regenerated ferric–brine solution to remove the impurities that have built up, e.g. zinc.

U.S. Bureau of Mines Process

In this process[28] (Fig. 13), galena concentrate is leached in a solution of ferric and sodium chlorides at 95°C to produce lead chloride, which is separated from the leach residue by filtration. The lead chloride is crystallized selectively from the solution, and the crystals are separated from the solution, washed in a centrifuge, and dried. The crystals are then fed to a bipolar fused-salt cell utilizing an electrolyte of lead and lithium chlorides. The cell is operated at 450°C, with molten metallic lead being deposited on the cathodic site and chlorine gas being evolved at the anodic site:

$$\text{Cathode:}\quad Pb^{2+} + 2\,e \rightarrow Pb(l)$$
$$\text{Anode:}\quad 2\,Cl^- \rightarrow Cl_2 + 2\,e.$$

The barren solution of zinc and sodium chlorides is regenerated to the ferric chloride–sodium chloride leaching solution by the bubbling of chlorine gas from the cell through a packed tower. The impurities that build up in the solution (e.g. zinc) must be removed by a bleed.

Lead Refining

The product of all lead smelters is crude bullion, which requires further refining to produce pure lead. The analysis of the bullion depends on the quality of the lead concentrate, a typical analysis of the bullion produced from South African concentrates being as follows:

Element	*Analysis*
Pb	98%
Cu	1,5%
Sb	0,15%
As	0,02%
Bi	0,03 to 0,10%
Ag	0,100%
Au	0,05 p.p.m.

Pyrorefining

Pyrorefining is the most common method employed, although electrolytic refining is done under special circumstances. Pyrorefining[29,30] (Fig. 14) is usually a batch

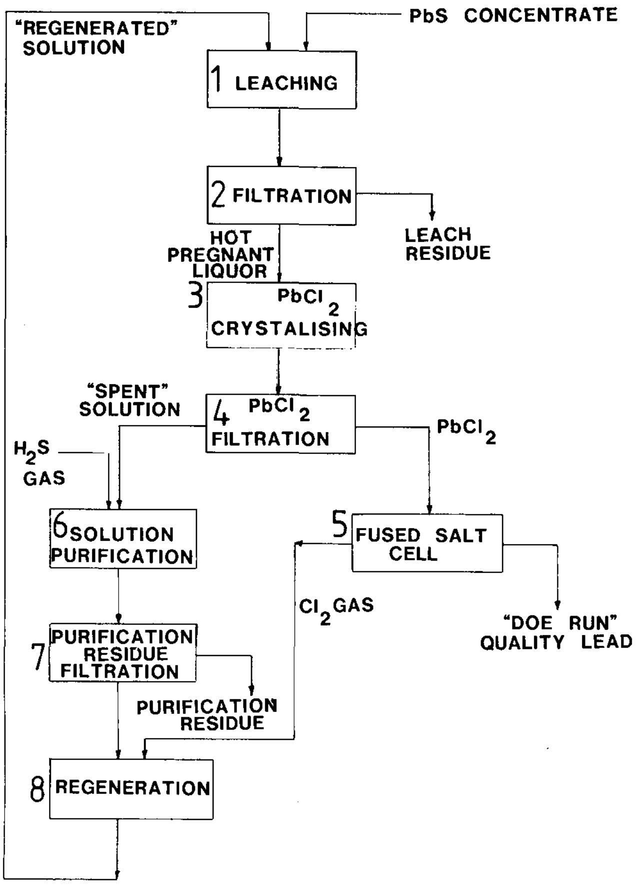

Fig. 13—U.S. Bureau of Mines lead process

process that is conducted in gas- or oil-fired kettles with a capacity of between 100 and 200 t of lead. The following steps are involved.

Drossing. Bullion is allowed to cool from 900 to 400°C, and the resultant copper-containing dross is skimmed off the surface and processed further in a reverberatory furnace.

Decopperizing. Sulphur is stirred into the bullion at 450°C, where it reacts with any copper present to form cuprous sulphide. The charge is cooled to 330°C, and the copper dross is skimmed off the surface.

Softening. In the softening process, arsenic and antimony are removed by the stirring of caustic soda and sodium nitrate into the molten lead. Arsenic, antimony, and tin are oxidized and the caustic skims can be removed from the refining kettles for further processing. Where the arsenic and antimony levels are high, the preferred method for their removal is the wet Harris process. Lead is pumped through molten caustic soda in a Harris machine, and oxidation of the impurities is controlled by the addition of sodium nitrate. The molten salt is treated in a wet-processing plant for the recovery of calcium arsenate, calcium stannate, and sodium antimonate.

Desilvering. This is referred to as the Parkes Process, in which silver, gold, and any remaining copper are removed by the addition of zinc. The process is based on the fact that zinc–silver–gold alloys are insoluble in lead saturated with zinc. Approximately 0,55 per cent zinc saturates the lead metal. Desilvering is done in two stages, and the resultant zinc–silver alloy is processed further to produce dore metal, which can be refined to produce pure silver.

Dezincing. The zinc remaining in the lead after desilvering is recovered by vacuum distillation at 580°C in a special kettle.

Trace refining. The lead is treated with caustic soda to remove trace metals such as arsenic, antimony, and zinc prior to the removal of bismuth.

Debismuthizing. For bismuth contents below 3,5 per cent, the Kroll–Betterton process is employed. This reduces the bismuth to below 100 p.p.m. The lead is saturated with calcium and magnesium metal, and an excess is added to combine with the bismuth and form $CaMg_2Bi_2$. The lead is cooled, and the crystals of calcium–magnesium–bismuth are skimmed off the surface. The bismuth content is built up by the recycling of part of the bismuth crust. The bismuth crust is processed to produce a lead–bismuth alloy containing 10 per cent bismuth, which is a saleable product.

Second-stage trace refining. This is the final refining stage, in which any residual trace metals (arsenic, antimony, copper, zinc) are removed, as well as the calcium and magnesium from the debismuthizing stage. The final lead product is normally cast into 45 kg pigs or 900 kg jumbo blocks.

A typical specification for pryorefined lead is as follows:

Lead	>99,99%
Cu	<2 p.p.m.
As	<2 p.p.m.
Sb	<2 p.p.m.
Sn	<2 p.p.m.
Zn	<2 p.p.m.
Cd	<2 p.p.m.
Fe	<2 p.p.m.
Bi	<80 p.p.m.
Ag	<4 p.p.m.
Maximum impurities	<100 p.p.m.

Electrolytic Refining

Where the bismuth content of the lead bullion is high, electrolytic refining (Betts Process) is practised[31]. The electrolytic cells are plastic lined, the anodes are cast-lead bullion, and the electrolyte is a solution of lead fluosilicate, $PbSiF_6$, and free fluosilicic acid. The cathode starting sheets are made from pure electrolytic lead.

All the impurities in the lead bullion are collected as anode slimes, which are processed further for the recovery of the individual metals (e.g. silver, bismuth, arsenic, antimony). The lead cathodes are washed, melted, drossed, and cast into ingots.

Occupational Safety and Health

For the past 500 years, lead has been extracted and worked as a metal or compound. As a result of industrialization in the last century and the massive increase in the health hazards involved, lead poisoning became a

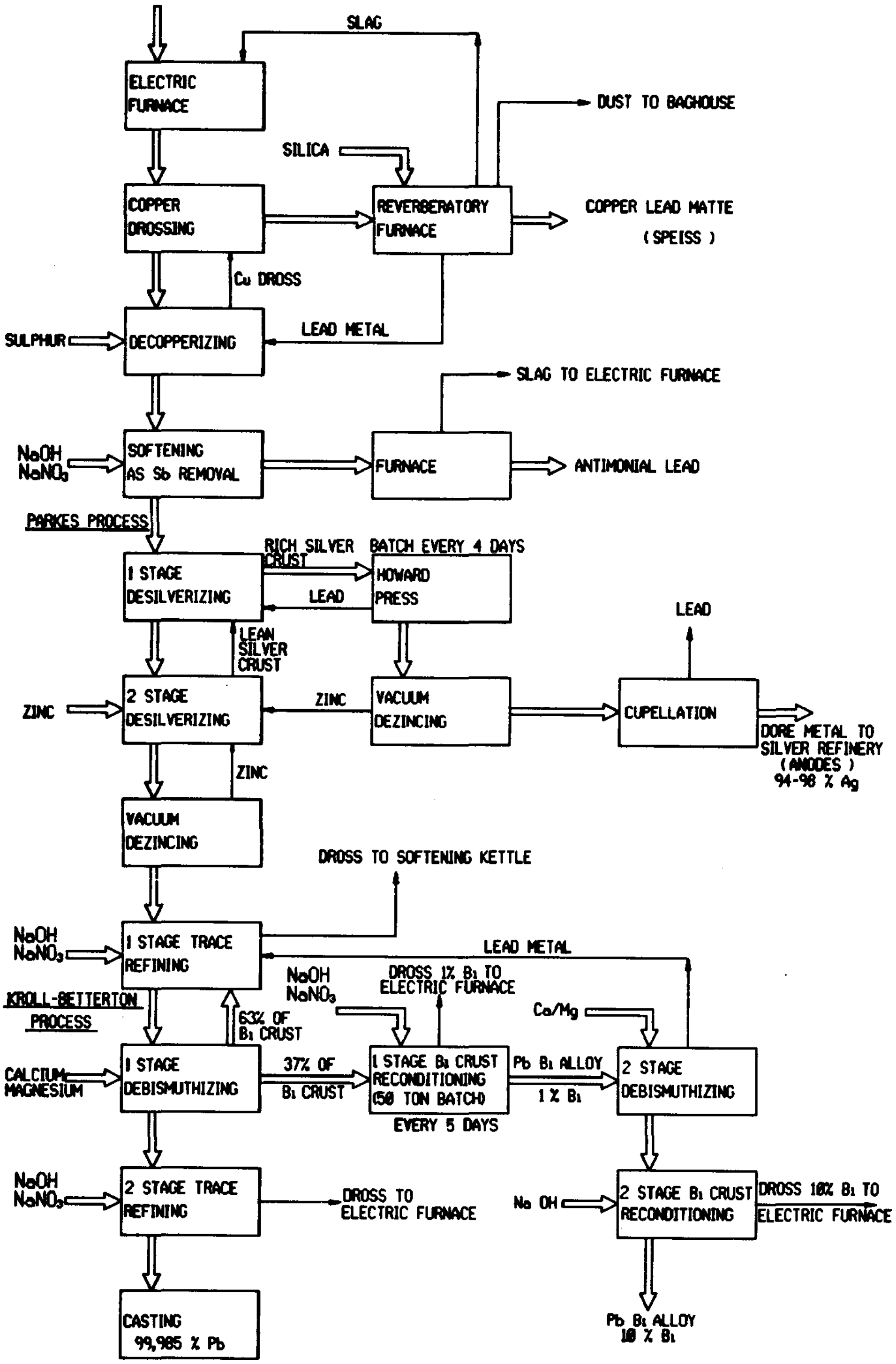

Fig. 14—Pyrometallurgical lead refining

classical heavy-metal poisoning and the subject of a vast amount of literature. It also became the subject of the first State controls in the field of industrial safety.

In the field of health protection, discussions and consequent action have led to comprehensive control of lead as a work hazard. Standards set for the work-place by State environmental agencies in Europe and the U.S.A. have been regarded as unrealistically stringent, and in many cases impossible to meet by the use of existing technology. However, precautionary medical examinations and blood tests in lead plants have made possible the prevention of practically all lead diseases.

Lead is taken into the human body via three major avenues: food (e.g. lead solder leached into canned food or lead picked up from the soil by plants), water (e.g. lead liberated from lead-containing water pipes), and air (mainly from vehicle emissions). Lead that is absorbed by the digestive organs or lungs circulates in the blood, accumulates temporarily in the liver and kidneys, and settles in the bones as a largely stable inert lead deposit.

The usual occupational lead poisoning resulting from an accumulation of absorbed lead gives rise initially to ill-defined general complaints such as stomach or intestinal disorders and a feeling of illness. Lead poisoning then develops in the form of an illness of varying severity with colic-type stomach pains and 'lead colouring'. Delayed disorders such as brain damage or lead cirrhosis of the kidneys are rarely encountered. Much is still to be learnt about the effects of lead, and what is needed is the confirmation of clinical suspicion with laboratory tests. It has been claimed that a lead content of more than 40 μg per 100 ml of blood can have an effect on the intelligence and activity level of children. Lead poisoning caused by the plumbing and aquaducts used by the Romans may have affected the minds of many, and it has been claimed that this contributed to the fall of the Roman Empire.

Excretion of lead takes place through the kidneys, gall bladder, hair, nails, and pores in the skin (perspiration). Within limits, the excretion of lead can be adjusted to match an increase in the absorption of lead or in the lead concentration in blood.

Vehicle Emissions

As industrial lead hazards have been brought more and more under control, attention has become focused on the use of lead in gasoline, which is regarded as a source of environmental pollution. Speculation on the effects of lead from motor-car exhausts has been widespread. Unfortunately, the arguments presented have not always been based on scientific principles but have been of a highly emotive or political nature, and have given rise to a great deal of investigatory work.

In the 1960s much of the work was related to vehicle emissions and atmospheric lead. City populations generally have higher levels of lead in the blood than rural groups, but no definitive relationship between lead in the air and in the blood have been demonstrated. The atmospheric lead content in uninhabited areas was measured as 0,004 to 0,008 μg per cubic metre, compared with that in residential areas of large cities, which varied from 2 to 6 μg per cubic metre. It is estimated that 90 per cent of the lead in air originates from vehicle emissions. In 1969 in West Germany, 6 kt of lead were emitted by vehicles alone. The lead content of fuels was then gradually reduced by law from 0,4 to 0,15 g/l over the period 1971 to 1976, and it was claimed that the atmospheric lead values decreased by up to 65 per cent.

Atmospheric lead consists largely of lead oxide, which is the combustion product of tetraethyl lead as used in gasoline. The average particle size of this lead dust is 0,25 μm, which means that it remains airborne for long periods of time.

South Africa has the dubious honour of using petrol with the highest lead levels in the world (Table VIII).

TABLE VIII
LEAD CONTENT OF PETROL

Country	Lead, g/l
South Africa*	0,836
U.S.A.	0,29
Japan	0,31
France	0,40
United Kingdom	0,40
Germany	0,15
Italy	0,40

*Reduced to 0,6 g/l from February 1986

Pressure on the British government by environmentalists and health scientists was instrumental in the decision taken in 1983 to remove all lead from petrol by 1990. In late 1984, the E.E.C. countries decided that all new vehicles coming onto the market from 1989 are to burn only unleaded gasoline. The dealine set by the U.S.A. for the removal of lead from petrol was July 1985. It seems likely that lead will be phased out as an additive to fuel throughout the world over the next decade.

In South Africa, lead in the air is being monitored at approximately 22 sites, so that the problem can be evaluated quantitatively. It has been suggested that, because of its relatively small car population in relation to the vast size of the country, the situation has not yet been reached where lead emissions from motor vehicles constitute a risk to public health. Although the removal of lead from petrol is costly, it is likely that South Africa will follow the example of the U.S.A. and the E.E.C. countries.

Future Outlook

The world's demand for lead could reach 7,3 Mt by the year 2000—a 39 per cent increase on 1983's 5,24 Mt. This is according to a report on lead published by the U.S. Bureau of Mines in 1985. The total U.S. demand, which stood at 1,14 Mt in 1983, is forecast to rise to 1,6 Mt in the year 2000.

Markets in Central and South America, Africa, and the Middle East are expected to offer better prospects for lead in the next decade than the traditional markets of Europe and the U.S.A. Projects in Italy and Peru and those known to be under consideration in Morocco, India, Iran, Taiwan, and Canada will increase lead capacity in the future.

Because concern about environmental pollution has resulted in legislation to reduce certain dissipative uses of lead, e.g. lead in petrol and paints, a growing proportion of lead will be used in non-dissipative applications, in which the bulk of the metal can be recycled. The implications are that the production of secondary lead will increase in proportion, and it is predicted that this production will increase in the U.S.A. to 56 per cent of the total, as against the 1983 figure of 39 per cent. This trend can be expected throughout the world.

Although the current outlook in regard to markets for lead is relatively pessimistic, the situation in the longer term is not one of unrelieved gloom. The long-term outlook is very dependent on the development of new markets or the expansion of existing markets.

Two potential new markets have been identified for lead in the form of organic compounds. These are paved asphalt roads and roofing material, in which the lead-bearing material slows the oxidation of asphalt and extends it life by up to 100 per cent. Field trials are under way to prove its effectiveness and environmental safety.

In regard to the expansion of existing markets, the use of the lead–acid battery is receiving much attention. Long-term developments include battery-powered airport support equipment, uninterruptible power-supply systems, and electrical-load levelling. Despite much research, very few new uses for lead have emerged in recent times.

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Materials engineering

In a major new initiative, The Institute of Metals is developing a series of international conferences and associated exhibitions in the field of materials engineering. The first of these events will be MATERIALS '87—Processing and Property Control, which is to be held in London from 13th to 15th May, 1987.

MATERIALS '87, organized in association with a number of other bodies, will bring together an international gathering of scientists, technologists, and engineers from industry and the academic world concerned with the control of materials structure and properties through processing.

An important aim of the Conference is cross-fertilization between the different specialist fields dealing with metals, ceramics, polymers, and composites. A comprehensive programme of keynote addresses and papers presenting the results of research and development will enable delegates to broaden their knowledge of materials outside their specialist spheres.

The subjects covered will range from fundamental considerations of structure and property control to technological aspects of materials process engineering.

The papers presented will deal with the following seven process areas:

- *Solidification*: near-net-shape forming; fusion cast ceramics; metallic glasses; nickel-based superalloys
- *Powder processing*: ceramics; powder consolidation; magnetic materials; aluminium alloys; rapidly solidified powders; liquid-phase sintering
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- *Surface engineering*: treatments of ceramics, glass, polymers, and metals; high-energy density treatments, etc.
- *Joining*: adhesive bonding of metals, ceramics and polymers; electron-beam and laser welding; fusion, solid phase, and adhesive bonding
- *Production and processing of composites*: polymer and metal matrix composites
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