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(54) HYDROMETALLURGICAL RECOVERY OF LEAD FROM  
MIXED METAL SULPHIDES

(71) We, SOCIÉTÉ MINIERE ET METALLURGIQUE DE PENARROYA, a French Société Anonyme, of 1 Boulevard de Vaugirard, 75751 Paris, Cedex 15, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a hydro-metallurgical process for the treatment of metal sulphides containing lead. It relates more specifically to a process for selective solubilisation of lead as compared to other non-ferrous metals and iron contained in such sulphides.

It is known that galena, or lead sulphide, is frequently found in the natural state in other sulphides such as pyrites, blende, copper sulphide and the sulphides of non-ferrous metals.

According to the conventional metallurgical processes, the different sulphides forming part of the ore are separated by differential flotation, and then treated by conventional pyrometallurgical processes. Nevertheless, differential flotation does not always give a perfect separation; the concentrates obtained may then be either concentrates as such, or mixed concentrates, or concentrates of very impure lead whereof the proportion of lead is no more than 40 or 50% instead of the more usual 60 to 80%.

The above concentrates are very difficult to process in accordance with the techniques developed in conventional metallurgy; we have recently made some improvements in the processing of complex ores and flotation concentrates.

Our British Patent Specification No. 1,478,571 describes a process for the solubilisation of all the non-ferrous metals contained

in a sulphide compound by means of cupric chloride regenerated by means of air and of a regenerating agent which may be hydrochloric acid or ferrous chloride.

The processing of the solutions thus obtained, if they contain zinc, is described in our British Patent No. 1,502,404, namely lead may be separated from the other non-ferrous metals by precipitating its chloride by cooling the solution. The lead chloride thus obtained is very pure; in particular, it contains no more than small quantities of bismuth whereof the separation from lead is always difficult. The lead chloride may then be cemented by more reducing metals than itself, such as zinc or iron, for example. However, despite numerous advantages, this technique is sometimes costly and is not very appropriate for the efficient working of deposits of lead sulphide. Also, this method requires the presence of a plant for precipitation of lead chloride and has a heat balance which is not always favourable.

This is why it is an object of the present invention to provide a method of treating an ore or concentrate containing lead sulphide and other metal sulphides which renders it possible to obtain a solution of lead chloride free of other metals and especially which is as selective as possible with respect to the other non-ferrous metals.

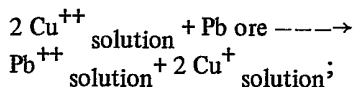
Another object of the present invention is to provide a method of processing the solution obtained from this selective action.

The invention provides a hydrometallurgical process for the treatment of an ore or concentrate containing a mixture of metal sulphides including lead sulphide, wherein the ore or concentrate is contacted with an aqueous solution containing at least one chloride selected from the chlorides of copper, bismuth, antimony,

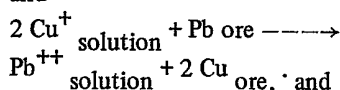
arsenic and silver, the quantity of the chlorides used being not more than 120% of that which is stoichiometrically required for the total dissolution of the lead contained in the sulphide compound; 100 or 110% may often be adequate.

One of the principal uses of the present invention consists in the selective lixiviation of the lead contained in a sulphide compound; cuprous and cupric chlorides are preferably used and hereinafter the invention will be principally described by reference to the use of copper chloride, but the chlorides of silver, bismuth, arsenic and antimony can be used in similar manner. (The term "lixiviation" means the leaching of the lead from the ore by the chloride solution.)

The lixiviation is performed at a higher temperature than ambient temperature, preferably between 60°C and the boiling point of the reaction mixture. By virtue of the presence of the copper in limited quantity during this lixiviation, the dissolution of the lead results not only from the action on its sulphide by cupric chloride to give plumbous chloride and cuprous chloride, but also an exchange between the cuprous cations of the solution and the lead of the sulphidised compound. If the lixiviation is performed solely by means of copper chlorides, two reactions occur, shown as follows:



and



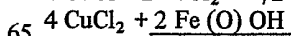
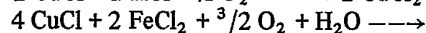
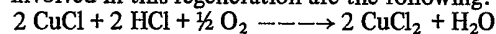
the limitation on the quantity of cupric chloride used may consequently be expressed as:

$$[\text{Cu}^{++}] + 2 [\text{Cu}^{+}] \leq [\text{Pb}^{++}] \times 1.2$$

the three expressions refer to the respective molar amounts of cupric copper and cuprous copper present initially and of the lead present initially in the sulphide compound and able to pass into solution.

The lixiviation may be carried out in a single reactor or in a moving bed or in several consecutive reactors in which the sulphide compound(s) is displaced in counterflow to the attacking solution.

The cupric chloride may be regenerated partially *in situ* or concomitantly with the lixiviation by the method claimed in our aforesaid British Patent No. 1,478,571. This regeneration, which may be performed *in situ* or in a separate reactor, consists in oxidising the cuprous ions in the presence of hydrochloric acid and/or of ferrous chloride; the reactions involved in this regeneration are the following:



↓

In the regeneration, the condition applicable to the quantity of chlorides placed in operation may be expressed in the following manner: the quantity of chloride ions present initially in the form of a chloride of copper, bismuth, antimony, arsenic, silver, ferrous iron and/or of hydrogen, should not be more than that which would be in the form of lead chloride if all the lead present in the sulphide compound were in the form of plumbous chloride.

The selective lixiviation may be used to give either a sulphide compound containing practically no lead, or else to directly give as pure a lead chloride solution as possible. In the first case, it is preferable to lixivate with as great a quantity of copper chloride as possible, e.g. 120% of the stoichiometric amount, although even when complete dissolution of lead is desired, it is better to use an amount as close as possible to the stoichiometric amount of copper chloride, to obtain the best selectivity. In the second case (to give a solution) it is preferable to lixivate with less than the stoichiometric quantity of chloride (preferably cupric).

Depending on the dissolving capacity of the aqueous lixiviating solution, the lead chloride may be obtained in the form of a solution or of a pulp.

In the first case, to ensure the retention in solution of the lead, the concentration of chloride ions in the aqueous phase is preferably at least 2 gram-equivalents per litre of chloride ions, more preferably greater than 4 gram-equivalents per litre disregarding the chlorides used for the lixiviation.

These chloride ions may be added in the aqueous phase in the form of ammonium chloride or a chloride of a water-soluble metal chloride, especially of an alkali or alkaline earth metal.

In the second case, recovery in the form of pulp is sufficient for the quantity of lead to be lixiviated per unit of volume to be greater than the dissolution capacity of the lixiviating solution.

The products of the lixiviation are (a) a saturated lead chloride solution possibly containing a small quantity of zinc chloride, (b) crystalline lead chloride and (c) a solid mixture of copper sulphides, mainly cupric sulphide, and also sulphides of the metal(s) whereof the chloride was used to treat the lead sulphide, and metal sulphides which had not reacted with that solution.

We have surprisingly found that the presence of the crystallised lead chloride phase does not in any way impede the lixiviation reaction, despite the fact that the crystals of plumbous chloride are dispersed and are intimately mixed with the sulphides, and tend to cover the particles of ore or of concentrate.

One of the principal advantages in this second embodiment is that it allows the use of concentrated copper chloride solutions, having a copper concentration of at least 30 g/l, or

0.5 M. To avoid increasing the solubility of the lead chloride, the concentration of free chloride ions, excluding the chlorides needed for the lixiviation, it preferably not greater than 2 and more preferably between 0.5 and 1.5 gram-equivalents per litre. The chloride ions may be supplied in the form of wholly or partially dissociated chlorides; only wholly dissociated chloride is considered in the determination of the quantity of chlorides to be added.

The solid mixture resulting from the reaction should be treated, during which the pH value is preferably kept at not greater than 3, to separate the lead chloride from the residual sulphides. Examples of suitable physical treatments currently used in metallurgy during the production of concentrates from ores are flotation, separation in a dense medium and elutriation.

Another separation method consists in cementing into a pulp the solid mixture by means of a metal more reducing (electro-positive) than lead, such as iron or zinc, thus obtaining metallic lead which can easily be separated from the sulphide phase by use of one of the physical separation techniques described above; the pulp may be either the reaction mixture after being attacked by the chloride solution, or may originate from the conversion into pulp of the cake obtained after filtering and optional washing of the reaction mixture.

A third separation method consists in dissolving the cake of lead chloride and sulphide obtained after filtering and optional washing of the reaction mixture in a solution of dissociated metal chloride, to dissolve the lead chloride and separate it from the other solids.

Preliminary contacting of the sulphide compound with cupric or ferric chloride is preferred since it activates the ore, that is to say it distinctly increases the selectivity and speed of the lixiviation. In a first stage, this contact modifies the surface condition, and in a second stage modifies the sulphur concentration of the sulphide compound by dissolving a part of the lead. This favourable modification may equally be obtained whilst having sulphur in the residual mixture. Since cupric chloride forms part of the chlorides able to lixiviate lead selectively, its use is preferred to ferric chloride; treatment with cupric chloride makes it possible to simultaneously activate the ore and to perform the selective lixiviation.

The selectivity obtained by the present invention is the more remarkable in that it is applied with respect to less reducing metals than lead, such as bismuth, more reducing metals such as zinc, and to metalloids such as arsenic.

Bismuth, arsenic and even copper and silver are among the most difficult impurities of lead and should be eliminated from a lead solution if it is wished to perform a direct cementation. The process of the present application thus

makes it possible to selectively lixiviate the lead contained in the sulphide compound from the ore or concentrate by means of its own impurities; the process may equally be applied to eliminate particular impurities such as silver, bismuth, arsenic or copper from the lead chloride solutions.

The ease of absorption of these impurities by the ore varies with the concentration of copper ions of the solution which is to be purified. The purities obtained are remarkable. The lead contained in the ore or concentrate should be in greater quantity than that which is required stoichiometrically to precipitate these impurities in the form of sulphides. This purifying technique is well suited to lead chloride solutions obtained from treatment with ferric chloride.

The lead present as chloride in the solution thus obtained may be recovered by methods, for example, as disclosed in our British Patent No. 1,502,404. Recovery techniques which make it possible to obtain the cupric chloride regeneration agents directly or indirectly, that is to say hydrochloric acid and/or ferrous chloride are however preferable.

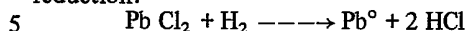
One recovery method is cementation by means of iron (which yields ferrous chloride), or of zinc (which yields zinc chloride which may be at least partially pyrohydrolysed into zinc oxide and hydrochloric acid). Iron preferably in the form of pre-reduced iron, is preferred for performing the cementation; the term "cementation" is used herein to include its technical equivalents such as (a) soluble anode electrolysis (the metal forming the anode being different from that to be recovered) and (b) use of cells of the "Daniell cell" type, which may be considered as a cementation of copper by means of zinc. In these two cases, the electrodes may be separated by a partition permeable to chloride ions.

Another recovery method is reduction of lead chloride by hydrogen; this may be performed in accordance with the general technique of reduction of metal chlorides by means of hydrogen known under the name "van Arkel process". Another method is described as follows: the lead chloride obtained after the attacking action is recovered in crystallised form, for example by cooling the solutions charged with lead chloride. The lead chloride is then melted and then reduced by means of hydrogen, used either pure or diluted in an inert gas, such as nitrogen or a rare gas.

Reduction of the molten lead chloride is preferably carried out at a temperature between 700° and 950°C, and more preferably between 850° and 950°C; the pressure is most conveniently atmospheric pressure.

One of the preferred and surprising methods of carrying out this reduction consists in melting the lead chloride in a bath and blowing hydrogen into the bath by means of lances. The hourly rate of flow of hydrogen is preferably at

least twice the stoichiometrical quantity required to reduce all of the lead chloride, the stoichiometry corresponds to the following reduction:



The gases emerging from the reduction thus contain both the unreacted fraction of the hydrogen and the hydrochloric acid formed during the reaction. The hydrogen may be burnt to heat the lead chloride; the hydrochloric acid mixed with the hydrogen can be separated either before or after the combustion and can be recycled to the lixiviating process for the dissolution of the lead.

The hydrogen may also be recycled to the reduction of lead chloride after having been separated from hydrochloric acid in accordance with a conventional technique such as gaseous diffusion or cooling followed by an absorption in water.

The use of this reaction is surprising because thermodynamic calculations demonstrate that the reduction reaction is very difficult; the standard free enthalpy variations ( $\Delta G$ ) are greater than or equal to nought at the different temperatures contemplated, as shown in the following table:

Temperature	$\Delta G$ Kilocalories/mole
900°C	0
827°C	+4
527°C	+11

These calculations of enthalpy variations were made on the basis of the tables and graphs published in "The thermochemical properties of the oxides, fluorides and chlorides to 2500°K", by Alvin Glassner — Report ANL (Argonne National Laboratory) — 5107.

The sulphide residue from the purification or from the lixiviation of the ore or concentrate may be processed so as to recover the non-ferrous metals present, e.g., by one of the techniques described in our British Patents Nos. 1,478,571, 1,497,349, 1,497,350 and 1,502,404.

The application of the process in accordance with the present application renders it possible to improve and/or extend the sphere of application of the processes described in these prior patent specifications. These processes may make use of the ferrous chloride produced during the cementation of the lead for the regeneration of the cupric chloride, and may provide the solutions of chloride required for lixiviation.

The invention will now be described with reference to the accompanying drawing, the single figure of which is a flow sheet of an embodiment of the process of the invention including regeneration of the chloride solution.

In this figure, the paths of the solids are illustrated by means of a double line and those of the liquids by means of a single line.

The mixture of sulphides including lead sulphide, to be treated is fed into a selective

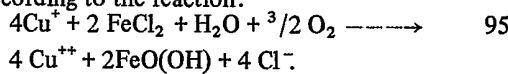
action reactor 1 in which it is contacted with a solution of copper chloride, the origin which is described subsequently.

The lead chloride solution thus obtained is passed into a cementation plant 2, whilst the residual sulphide is passed into another reactor 4 in which it is placed in contact with a solution of cupric chloride and in which all the non-ferrous metals present are dissolved.

In the cementation plant 2, the lead chloride solution is placed in contact with metallic lead or with a more reducing metal than lead, the residual impurities nobler than lead then being precipitated in metallic form.

The lead chloride solution emerging from the plant 2 is passed into another cementation plant 3 in which it is placed in contact with a more reducing metal than lead, preferably iron. The lead then precipitates in metallic form and the reducing metal (e.g. iron) passes into solution in the form of ferrous chloride.

The ferrous chloride solution emerging from the plant 3 is mixed with the solution of chlorides of non-ferrous metals emerging from 4 and is conveyed into a plant 5 for regeneration of the cupric chloride by bubbling of air or of a gas containing oxygen, the ferrous chloride being precipitated in the form of goethite according to the reaction:



Supplementary quantities of ferrous chloride and possibly of hydrochloric acid may also be fed into the plant during the process.

The recovered solution of cupric chloride is separated into two parts by means of a valve 6: one part is used as the cupric solution in the reactor 1 in such quantity that the dissolution of the lead is selective and the remainder is passed into the reactor 4.

Arsenic, as well as a part of the bismuth and of the antimony which are possibly put into solution, are eliminated during the stage of precipitation of goethite, arsenic in the form of ferric arsenate and bismuth and antimony in the form of oxychlorides.

One may incorporate a procedure of this kind in one of the processes described in our British Patents Nos. 1,478,571, 1,495,854, 1,497,349, 1,497,350 and 1,502,404 and thereby improve such process. If reference is made to the graphs of some of these applications, the plants bearing the references 4 and 5 in the present application correspond respectively to the plants 2 and 6 of Figure 1 of the British Patent No. 1,497,350 and to the plants A and E of the British Patent No. 1,502,404.

The following examples illustrate the invention. Percentages are by weight unless otherwise specified.

**EXAMPLE 1** Lixiviation of a lead concentrate by means of cupric chloride ( $\text{CuCl}_2$ ) with dissolution of the

		lead and precipitation of the copper.		and topped by a reflux condenser.					
		A volume of 6.00 litres of a lixiviating solution containing 250 g/l of sodium chloride and		428.2 g of a finely crushed lead concentrate, containing 45.1% of lead and 5.83% of zinc in the form of sulphides, is then added to the					
5	9.76 g/l of copper in the form of cupric chloride is maintained at the temperature of 80°C in a spherical flask equipped with a heating system			above solution. The mixture of solid and liquid is shaken vigorously for two hours and then filtered, giving the following analysis:				70	
10	<b>Description</b>	<b>Weight (g) or volume (ml)</b>	<b>Zn g/l -%</b>	<b>Total Zn g</b>	<b>Cu g/l %</b>	<b>Total Cu g</b>	<b>Pb g/l -%</b>	<b>Total Pb g</b>	75
	initial lead concentrate	428.2 g	5.83%	25.0	1.42%	6.1	45.1%	193.1	80
15	initial solution	6000 ml	0.06g/l	0.36	9.76g/l	58.6	less than 0.02g/l	0	
20	TOTAL INPUT			<u>25.36</u>		<u>64.7</u>		193.1	85
	final solution	5800 ml	0.72g/l	4.18	1.82g/l	10.6	31.1g/l	180.4	
25	final solid	270.7 g	7.95%	21.5	20.6%	55.8	3.0%	8.1	90
	TOTAL OUTPUT			<u>25.68</u>		<u>66.4</u>		<u>188.5</u>	
30	yield of dissolution %			<u>14.0</u>				95.7	95
This example clearly shows that almost all the lead goes into solution, and the copper is precipitated.									
35	EXAMPLE 2. Further treatment of the residue of Ex <sub>1</sub> 1 and recovery of the precipitated copper.			condenser. 27.2 grammes of the final solid obtained in Example 1 is then added to this solution and is stirred in a homogeneous manner for two hours followed by filtration; the cupric ion concentration in the solution reaches 6.35 g/l during this period.				100	
40	Two litres of a lixiviating solution of cupric chloride containing 9.08 g/l of copper is kept at 80°C in a glass reactor topped with a reflux			The analysis is as follows:				105	
45	<b>Description</b>	<b>Weight (g) or volume (ml)</b>	<b>Zn g/l -%</b>	<b>Total Zn g</b>	<b>Cu g/l -%</b>	<b>Total Cu g</b>	<b>g/l -%</b>	<b>Total Pb g</b>	110
	initial solution	2000 ml	0.06g/l	0.12	9.08g/l	18.16	less than 0.01g/l	0	
50	incoming solid	27.2 g	7.95%	2.16	20.6%	5.6	3.0%	0.82	115
	TOTAL INPUT			<u>2.28</u>		<u>23.76</u>		<u>0.82</u>	
55	final solution	2000 ml	0.72g/l	1.44	11.54g/l	23.1	0.54	1.08	120
	final solid	17.3 g	4.52%	0.78g	1.92%	0.33g	0.35%	0.06	
60	TOTAL OUTPUT			<u>2.22</u>		<u>23.41</u>		<u>1.14</u>	125
65	This experiment shows that the second lixiviation treatment allows the recovery of the copper precipitated during the first treatment and the dissolution of a large proportion of the			zinc and of the lead which were not dissolved during the first (selective) treatment. If the chemical composition of the residue from the second treatment is compared to the initial				130	

composition of the ore, it is seen that the overall yield of dissolution of the metals for the two treatments is:

5	zinc	: 68.9%
	lead	: 99.7%
	copper	: 46.3%

The recovery of close to half of the copper initially present in the concentrate is thus added to the total re-dissolution of the copper precipitated during the selective treatment.

EXAMPLE 3. Purification of a lead chloride solution by precipitation of the impurities.

This experiment was performed on an aliquot part of the solution obtained in the Example 1. 4 grams of lead powder is added in one batch to 500 ml of this solution kept at 80°C and stirred vigorously. The stirring is continued for 70 minutes, followed by a solid-liquid separation by filtering, giving an analysis as follows:

15		Weight (g) volume (ml)	Zn g/l- %	Cu g/l- %	Pb g/l- %	As g/l- %	Bi g/l- %	Ag g/l- %	Sb g/l- %	80
	initial solution	500	0.72	1.82	31.1	0.118	0.01	0.045	0.01	
20	initial lead powder	4			100					85
25	final solution	500	0.59	0.026	32.0	0.032	0.005	0.002	0.01	90

It is observed that at the end of this operation, the solution is freed of the principal impurities, particular of copper and bismuth and partially of arsenic, liable to be entrained into a subsequent cementation of the lead; these impurities accumulate in the previous cement.

EXAMPLE 4. Cementation of the lead by means of iron sponge, from a solution of plumbous chloride (PbCl<sub>2</sub>) in a brine.

The solution originating from the pre-

cementation shown in Example 3 above is taken again for this experiment.

4.3 grams of iron sponge containing 72.4% of metallic iron crushed beforehand to a grain size of between 80 and 200 microns is added to 420 ml of this solution. The operation is performed whilst stirring vigorously at the temperature of 80°C for 100 minutes.

At the end of the operation, a solid-liquid separation is performed, giving an analysis as follows:

40	Description	weight (g) volume (ml)	Zn %- g/l	Cu %- g/l	Pb %- g/l	Fe %- g/l	As %- g/l	Bi %- g/l	Ag %- g/l	Sb %- g/l	105
45	precemented solution	450 ml	0.59	0.03	32.0		0.032	0.01	0.005	0.005	110
	iron sponge	4.3 g				97.0%					
50	final solution	400 ml	0.58	0.04	9.76	5.94	0.003	0.01	0.001	0.01	115
55	final cement	11.6 g	0.014	0.11	79.5	11.0	not determined	0.02	0.0025	0.005	120

EXAMPLE 5. Dissolution of lead by means of cuprous chloride (CuCl).

Two litres of a solution containing 16.5 g/l of cuprous ions and 22.1 g/l of copper are fed into a cylindrical reactor. This solution being kept at 80°C, consecutive fractions of lead concentrate are fed in.

After each addition of concentrate, the stabilisation of the concentration of cuprous ions is awaited before proceeding with another addition of ore. This procedure is followed until the complete disappearance of the cuprous ions. The results are summarised in the following table.

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	weight (g) vol. (cm <sup>3</sup> )	(Zn) g/l-%	Total Zn g	(cu) g/l-%	Total Cu g	(Pb) g/l-%	Total Pb g	(As) g/l-%	Total As g	(Bi) g/t	Total Bi g	(Ag) g/t	Total Ag g
initial concentrate	410.9 g	5.83%	24.0	1.42%	5.8	45.1%	185.3	0.36%	1.5	403	0.17	738	0.3
initial solution	2000 cm <sup>3</sup>	0.08g/l	0.16	22.1g/l	44.2	0.2g/l	0.4	—	—	—	—	—	—
total input	—	—	<u>24.16</u>	—	<u>50.0</u>	—	<u>185.7</u>	—	1.5	—	0.17	—	0.3
final solution	2000 cm <sup>3</sup>	2.76g/l	5.52	5.28g/l	10.56	15.4g/l	30.8	—	—	—	—	—	—
residue (damp)	443 g	4.25%	18.8	8.65%	38.3	35%	155.1	0.34%	1.5	384	0.17	619	0.27
total output	—	—	<u>24.32</u>	—	<u>48.86</u>	—	<u>185.9</u>	—	1.5	—	0.17	—	<u>0.27</u>
dissolution yield %	—	—	22.3	—	—	—	16.6	—	0	—	0	—	10

N.B. The true yield of lead chlorination is actually higher, a part of the PbCl<sub>2</sub> remaining within the residue as a consequence of the saturation of the solution.

The data shows the selectivity of the attack with respect to bismuth, silver and arsenic.

EXAMPLE 6. Influence of temperature; attack of the ore by the cuprous chloride (CuCl) at boiling point.

The reduced solution is heated to boiling point before the addition of the ore; boiling is maintained for 5 hours. The following table gives the results of this operation:

	weight (g) vol. (ml)	(Zn)	Total Zn g	(Cu)	Total Cu g	(Pb)	Total Pb g	
initial solution	500 ml	0.04g/l	0.02	17.9g/l	8.95	less than 0.02	0	75
fresh concentrate	32.3 g	5.83%	1.58	1.42%	0.46	45.10%	14.57	
total input	—	—	1.90	—	9.41	—	14.57	80
final solution	500 ml	1.12g/l	0.56	12.88g/l	6.44	10.52g/l	5.26	
residue (estimated weight)	26 g	5.15%	1.34	12.7%	3.30	30.4%	7.90	85
total output			1.90		9.74		13.16	
dissolution yield %			29.5				40.0	90

EXAMPLE 7. Tests for activation of the ore by means of cupric chloride (CuCl<sub>2</sub>). The ore is initially subjected to an activation at 80°C, by means of a solution of cupric chloride containing approximately 18 g/l of copper, for 15 minutes. The quantity of cuprous chloride used is equal to 31.7% of the stoichiometrical

quantity (QS) required to dissolve the lead.

A lixiviating solution of cuprous chloride CuCl is then fed into the reactor in such volume that the lead initially added exceeds 1.1 QS with respect to the quantity of Cl<sup>-</sup> ions linked to the copper, which are introduced into the reactor.

	weight (g) vol. (ml)	(Zn)	Total Zn (g)	(Cu)	Total Cu (g)	(Pb)	Total Pb	
activating solution	90 ml	—	—	18.5g/l	1.67	—	—	105
lixiviating solution	410 ml	0.12g/l	0.05	22.3g/l	9.14	0.02g/l	0	
fresh concentrate	38 g	5.83%	2.22	1.42%	0.54	45.10%	17.12	110
total input	—	—	2.27	—	11.35	—	17.12	
final solution	480 ml	0.82g/l	0.39	8.6g/l	4.13	18.9g/l	9.07	115
residue	30.2 g	5.85%	1.77	16.4%	4.95	24.9%	7.52	
total output	—	—	2.16	—	9.08	—	16.59	
yield (%)	—	—	18.1	—		—	54.7	120

The improvement of the yield and of the selectivity with respect to zinc are evident from this data.

EXAMPLE 8. Attack within a pulp of a lead concentrate originating from Aznalcollar (Spain).

1762 grams of lead concentrate is fed into 4

litres of cupric chloride solution containing 54 grams of copper per litre, which corresponds to 85% of the stoichiometrical quantity required to convert all of the lead present in the ore into plumbous chloride. After one and a half hours of reaction, the reaction mixture is filtered to yield a filtrate and a cake, giving the following analysis:

130



element	ore	cake	filtrate	
lead	47%	33.4%	11.1 g/l	This experiment shows that it is possible to observe the speed of dissolution of lead chloride, since equilibrium is reached at the end of 20 minutes, and that 70% of the equilibrium is reached after 5 minutes. The copper which had been precipitated during the previous attacks remains practically insoluble.
5 zinc	4.94%	3.98%	1.37 g/l	70
copper	0.96%	9.10%	<0.02 g/l	EXAMPLE 10. Use of hydrochloric acid and air for leading chlorination residue.
10 iron	13.4%	not determined	1.46 g/l	75
silver	768 g/T	not determined	not determined	This experiment was performed in a 20-litre cylindrical reactor equipped with a special stirring system. This stirring system is a flotation impeller normally designed to perform ore enrichments and has the feature of ensuring an intimate contact between the gas and the mixture, thanks to a satisfactory dispersion of the gas, and to a substantial recirculation of the volume of gas present above the level of the liquid.
15 chloride	not determined	11.2%	not determined	80
(g/T = grams per metric ton).				
20	The lead chloride yield amounts to 80% with respect to the ore, and 95% with respect to the copper chloride initially placed in operation at the beginning, and the rate of zinc dissolution amounts to no greater than 6% and demonstrates the great selectivity of the treatment.			85
25	This experiment illustrates the possibility of chlorinating a lead concentrate whilst operating with a high proportion of solid and with a short residence time.			
30	EXAMPLE 9. Dissolution of lead chloride contained in a chlorination concentrate.			
	20 litres of a brine from previous examples and containing the following elements:			
35	NaCl	256 g/l		
	Pb	4.5 g/l		
	Zn	0.22 g/l		
	Cu	0.24 g/l		
	are kept at 90°C in a 20-litre reactor.			
40	2,000 g of a homogenised solid originating from a variety of chlorination experiments is added in one batch. The composition of this product is as follows:			
45	Pb	33.5%		
	Cl	8.73 g/T		
	Zn	3.24%		
	Fe	9.94%		
	Cu	9.24%		
	H <sub>2</sub> O	10.0%		
50	This dissolution of lead chloride over a period of time is shown in the following table:			
	Time (h. min.)	Zn g/l	Cu g/l	Pb g/l
55	0.00	0.22	0.24	4.5
	0.05	0.26	1.0	19.9
	0.10	0.26	1.0	23.1
60	0.20	0.30	1.0	26.3
	0.40	0.28	1.0	26.6
65	1.30	0.30	0.94	26.0
	20 litres of solution having the following composition:			
	Pb	<0.2 g/l		
	Cu	16.6 g/l		
	Zn	41.6 g/l		
	Fe	0.2 g/l		
	are heated to 80°C in the above.			
	1,100 g of a solid, obtained from an ore which had been chlorinated, the lead chloride formed redissolved and the liquor decanted, is added in one batch. This solid has the composition:			
	Pb	2.61%		
	Cu	18.7%		
	Zn	6.84%		
	Fe	19.2%		
	H <sub>2</sub> O	10%		
	Compressed air is fed into the mixture at a flow rate of 1240 l/h. A solid-liquid separation is made at the end of 10½ hours. After washing with distilled water, the residual solid weights 764 g, and its chemical composition is:			
	Pb	0.45%		
	Cu	0.99%		
	Zn	1.75%		
	H <sub>2</sub> O	16.6%		
	Based on this analysis, the rate of dissolution of the elements present initially in the solid was calculated as follows:			
	Pb	88.0%		
	Cu	96.3%		
	Zn	82.2%		
	It is thus shown that it is possible to recover the copper precipitated during the chlorination stage with a satisfactory yield, whilst assuring the recovery of the residual Pb and Zn.			
	EXAMPLE 11. Elimination of the impurities accompanying lead by crystallisation of lead chloride.			
	This Example shows the degree of purity which may be reached by lead chloride obtained by crystallisation.			
	An impure solution of lead chloride is filtered and then allowed to stand for 48 hours. The initial and final temperatures of the solution			

are 85°C and 16°C, respectively. The crystals obtained are separated by filtration.

The analyses of the initial solution and of the crystals obtained are specified in the following table:

Description	weight or volume	Pb % g/l	Cu % g/l	Fe % g/l	Zn % g/l	Bi % g/l	Ag % g/l	Sb % g/l	As % g/l	Sn % g/l
initial solution	850 l	23.2	2.02	0.22	1.32	0.028	0.044	0.034	0.02	0.003
crystals	13.5 kg	74.4	0.015	0.07	0.005	0.009	0.002	0.02	0.01	0.012

The purity obtained is of the order of 99.9%.

Operating method of Examples 12, 13 and 14:  
80g of slightly damp lead chloride (corresponding to 56 g of metallic lead) are melted in a quartz tube. Hydrogen is bubbled into the molten chloride bath through a quartz pipe.

The height of the molten chloride amounts to 5 cms, prior to reduction. The operating parameters and the results of the different examples are summarised in the following tables:

#### EXAMPLE 12.

temperature 800°C  
period 1 hr.  
hydrogen flow rate 30 l/hr  
weight of the residual slag (PbCl<sub>2</sub>) 0 g  
weight of the reduced lead 56 g  
yield 100%

The same result is obtained if the hydrogen is replaced by a hydrogen-nitrogen mixture containing 50% of hydrogen, the rate of flow of the gaseous mixture being equal to 30 l/hr, the reaction period being increased to two hours and the other conditions remaining unchanged.

#### EXAMPLE 13.

temperature 800°C  
period 1 hr.  
hydrogen flow rate 15 l/h  
weight of the residual slag (PbCl<sub>2</sub>) 31 g  
weight of the reduced lead 35 g  
yield 64%

#### EXAMPLE 14.

temperature 700 700°C  
period 1 hr.  
hydrogen flow rate 30 l/hr  
weight of the residual slag (PbCl<sub>2</sub>) 36 g  
weight of the reduced lead 28 g  
yield 52%

The lead purity obtained exceeds 99.99%: the proportion of different impurities in the lead is summarised in the following table:

Impurity	proportion in g/T
arsenic (As)	60
antimony (Sb)	30
copper (Cu)	2
tin (Sn)	2
silver (Ag)	traces (limits of detection)
bismuth (Bi)	traces (limits of detection)
zinc (Zn)	traces (limits of detection)

#### EXAMPLE 15. Purification of lead chloride solution.

The impure lead chloride solution is continuously contacted with a fresh concentrate containing lead sulphide in two twenty-litre reactors working co-currently. The operating conditions are as follows:

- Average size of the granules concentrate : 200 μm
- Concentrate flow rate : 788 g/h
- Lead chloride solution flow rate : 20 l/h
- pH : 1.7
- Temperature : 90°C
- Residence time : 2 hours.

The results of this purification are given in the following Table.

Composition of the concentrate (%)	Composition of the impure solution (g/l)	Composition of the purified solution (g/l)	Composition of the emergent solid (%)
lead (Pb)	64.3	13.7	28.3
zinc (Zn)	4.48	6.3	6.9
copper (Cu)	0.42	4.0	0.00153

iron	(Fe)	4.83	1.0	3.1	6.8	
silver	(Ag)	0.0919	0.04	less than 0.002	0.34	
5 sulphur	(S)	18.0	—	—	27.0	70
bismuth	(Bi)	0.030	0.02	less than 0.006	0.14	
10 arsenic	(As)	0.090	0.034	less than 0.002	0.14	75
15 antimony	(Sb)	0.31	0.018	less than 0.002	0.52	80
sodium chloride		—	250	250	—	

- 20 This Example shows that it is possible to obtain a very good purification by contacting impure lead chloride solution with ore or concentrate containing lead sulphide. Such a
- 25 purity allows direct electrolysis (with a soluble or insoluble anode) of the purified lead chloride solution to recover metallic lead. Ferrous chloride does not impede the purification of lead chloride dissolved in concentrated chloride
- 30 solution (more than 2N) by contact with fresh lead sulphide.
- WHAT WE CLAIM IS:
1. A hydrometallurgical process for treating an ore or concentrate containing a mixture of
  - 35 metal sulphides including lead sulphide, wherein the ore or concentrate is treated with an aqueous lixiviating solution containing at least one chloride selected from the chlorides of copper, bismuth, antimony, arsenic and silver,
  - 40 the quantity of the said chlorides used being not more than 120% of that which is stoichiometrically required for the complete dissolution of the lead contained in the sulphides.
  2. A process as claimed in claim 1, wherein
  - 45 the said aqueous solution contains at least 4 gram-equivalents of chloride ions per litre.
  3. A process as claimed in claims 1 or 2, wherein the quantity of chloride in said
  - 50 aqueous solution is not greater than that which is stoichiometrically required for the complete dissolution of the lead contained in the sulphide.
  4. A process as claimed in claims 1, 2 or 3, wherein the temperature of the aqueous
  - 55 solution is between 60°C and the boiling point of the reaction mixture.
  5. A process as claimed in any one of the preceding claims, wherein the pH value of the
  - 60 aqueous solution is not greater than 3.
  6. A process as claimed in any preceding claim, wherein the aqueous solution also contains at least one chloride selected from ammonium chloride, the chlorides of the
  - 65 alkaline metals and the chlorides of the alkaline earth metals.
  7. A process as claimed in any one of the preceding claims, wherein the ore or concentrate is activated, before said treatment, by means of ferric chloride and/or cupric chloride.
  8. A process as claimed in any one of the preceding claims, wherein the lead chloride solution resulting from the treatment is purified by being contacted with metallic lead.
  9. A process as claimed in any one of the preceding claims, wherein the lead of the lead chloride solution resulting from the treatment is recovered by cementation by means of a more reducing metal than lead.
  10. A process as claimed in claim 9, wherein the cementation is an electrolysis in which the
  - 100 anode is a soluble anode of a more reducing metal than lead.
  11. A process as claimed in claim 10, wherein the said more reducing metal is zinc or iron.
  12. A process as claimed in any one of the preceding claims, wherein the aqueous solution contains cupric chloride and the cupric chloride is subsequently regenerated by means of a
  - 105 regenerating agent and air.
  13. A process as claimed in claim 12, wherein the said regenerating agent is ferrous chloride produced by the cementation of lead by means of iron.
  14. A process as claimed in any preceding claim, wherein after the lixiviation, the residue
  - 115 of the ore or concentrate is processed in accordance with the process described in British Patent Application No. 1,502,404.
  15. A process as claimed in any one of claims 1 to 13, wherein after the lixiviation, the residue of the ore or concentrate is pro-
  - 120 cessed in accordance with the process described in British Patent Specification No. 1,497,349.
  16. A process as claimed in any one of claims 1 to 13, wherein after the lixiviation, the residue of the ore or concentrate is pro-
  - 125 cessed in accordance with the process described in British Patent Specification No. 1,497,350.
  17. A process as claimed in any one of claims 1, 4 to 8 or 12, wherein the quantity of
  - 130

- lead present in the ore or concentrate sufficiently great so that the aqueous lixiviating solution used becomes gaturated with lead.
18. A process as claimed in claim 17, wherein the concentration of the copper in the aqueous solution is not less than 30 grams per litre.
19. A process as claimed in claims 17 or 18, wherein the concentration of free chloride ions is not greater than 2 gram equivalents per litre.
20. A process as claimed in any one of claims 17 to 19, wherein the solid mixture of lead chloride and of sulphides obtained after filtration of the reaction mixture is subjected to a physical separation technique, so as to separate the lead chloride from the sulphides.
21. A process as claimed in any one of claims 17 to 19, wherein the pulp obtained after the contacting with the aqueous lixiviating solution is subject to a cementation by means of iron or zinc.
22. A process as claimed in any one of claims 17 to 19, wherein the mixture of lead chloride and sulphides obtained after filtration of the reaction mixture is returned to the state of pulp and cemented by means of iron or zinc.
23. A process as claimed in claim 21 or 22, wherein the metallic lead obtained after cementation is separated from the sulphides by a physical separation technique.
24. A process as claimed in any one of claims 17 to 19, wherein the solid mixture obtained after filtration of the reaction mixture is redissolved in a solution of dissociated metal chlorides to yield a solution of lead chloride and a solid phase consisting of sulphides.
25. A process as claimed in any one of claims 1 to 16, 20 and 24, wherein the lead dissolved into the solution is recovered in the form of crystallised lead chloride, and this lead chloride is melted and then reduced by means of hydrogen to metallic lead.
26. A process as claimed in claim 25, wherein the reduction is performed at a temperature of between 850° and 950°C.
27. A process as claimed in claim 15 or 26, wherein the hydrogen is diluted in an inert gas.
28. A process as claimed in any one of claims 25 to 27, wherein hydrogen is blown into the molten lead chloride.
29. A process as claimed in claim 28, wherein the hourly flow rate of hydrogen is not less than twice the stoichiometrical quantity required for the total reduction of the lead chloride.
30. A process as claimed in any one of claims 25 to 29, wherein the hydrogen contained in the gases emerging from the reduction is separated from hydrochloric acid formed during the reaction of the lead chloride and hydrogen and is recycled to the lead chloride reduction, the hydrochloric acid being recycled to the lixiviating solution for treating the ore or concentrate.
31. A process as claimed in any one of the preceding claims, wherein impure lead chloride solution is purified by contacting it with fresh sulphide ore and then electrolysing the purified lead chloride solution using an insoluble anode.
32. A process as claimed in claim 1 substantially as hereinbefore described with reference to any one of the Examples 1 and 5 to 8.
33. A process as claimed in claim 1, substantially as hereinbefore described with reference to the accompanying drawing.
34. Lead when recovered by a process as claimed in any preceding claim.
- GEE & CO.,  
Chartered Patent Agents  
Chancery House,  
Chancery Lane,  
London WC2A 1QU

