

- [54] **PROCESS FOR PRODUCING CADMIUM**
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 [51] **Int. Cl.**..... **C22b 17/00**
 [58] **Field of Search**..... 75/109, 121, 71; 204/119

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[57] ABSTRACT

Cadmium is recovered from a suspension of a CdSO_4 solution containing as impurities Co, Ni, Cu, As, Sb, Pb and Zn salts, and a solid phase containing Cu, As or Sb. A reducing agent, e.g., metallic Zn is added to the solution to cementate all impurities but Pb, which is precipitated from the filtered solution by means of adding thereto Sr or Ba salts. Finally Cd is cemented, separated from the solution and smelt refined with alkali to remove Zn.

6 Claims, 4 Drawing Figures

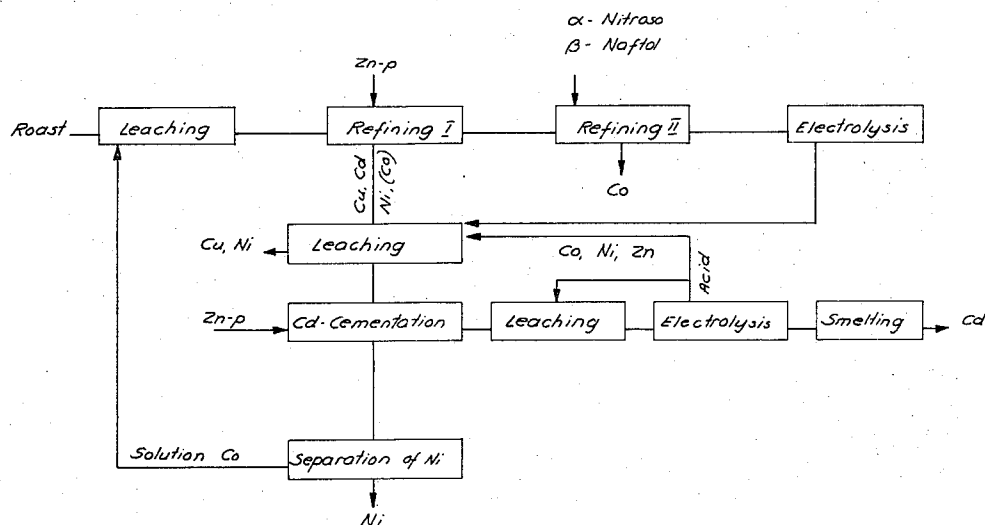


Fig. 1

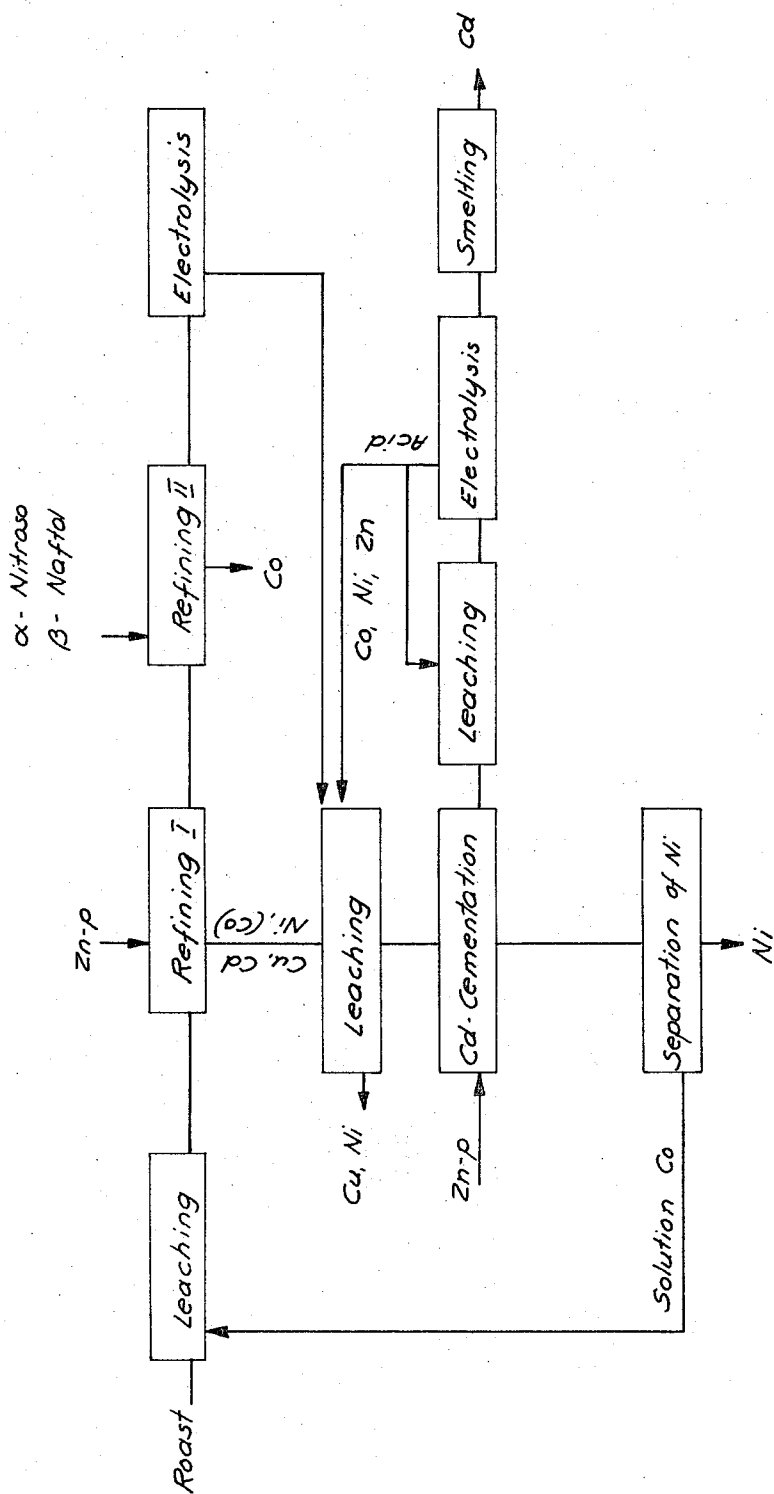


Fig. 2

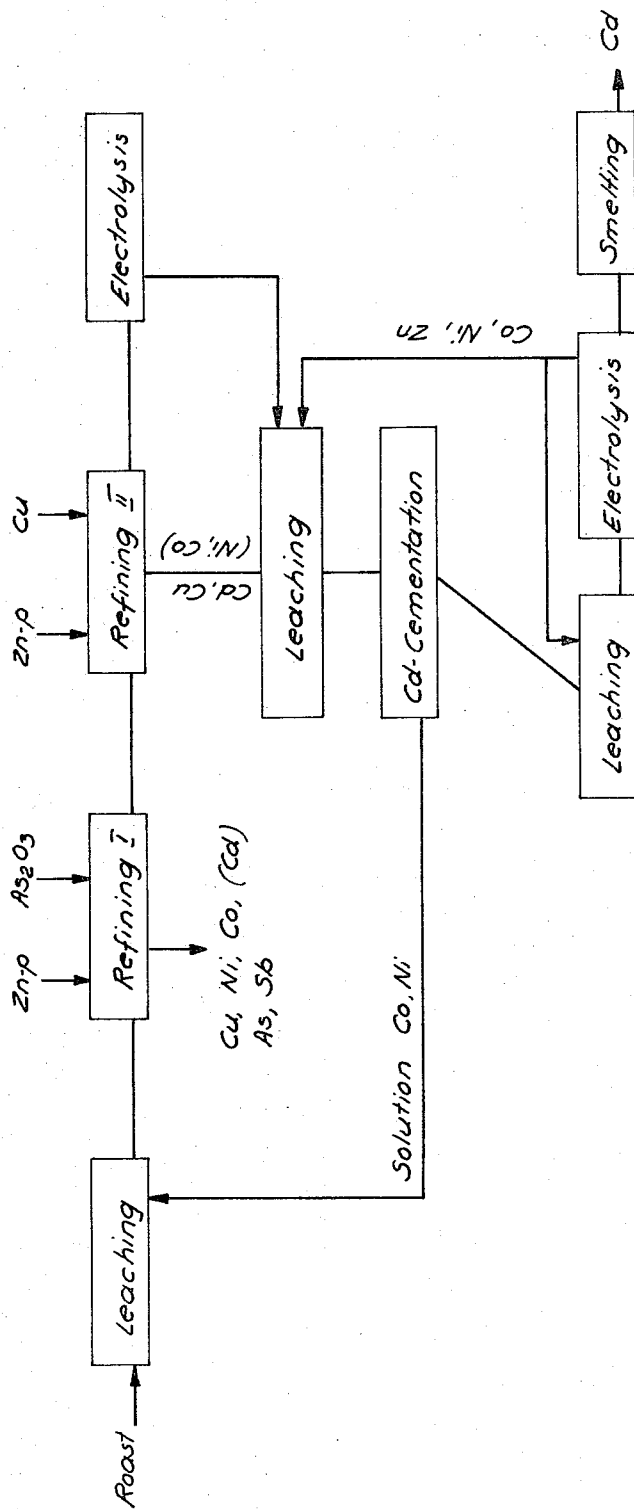


Fig. 3

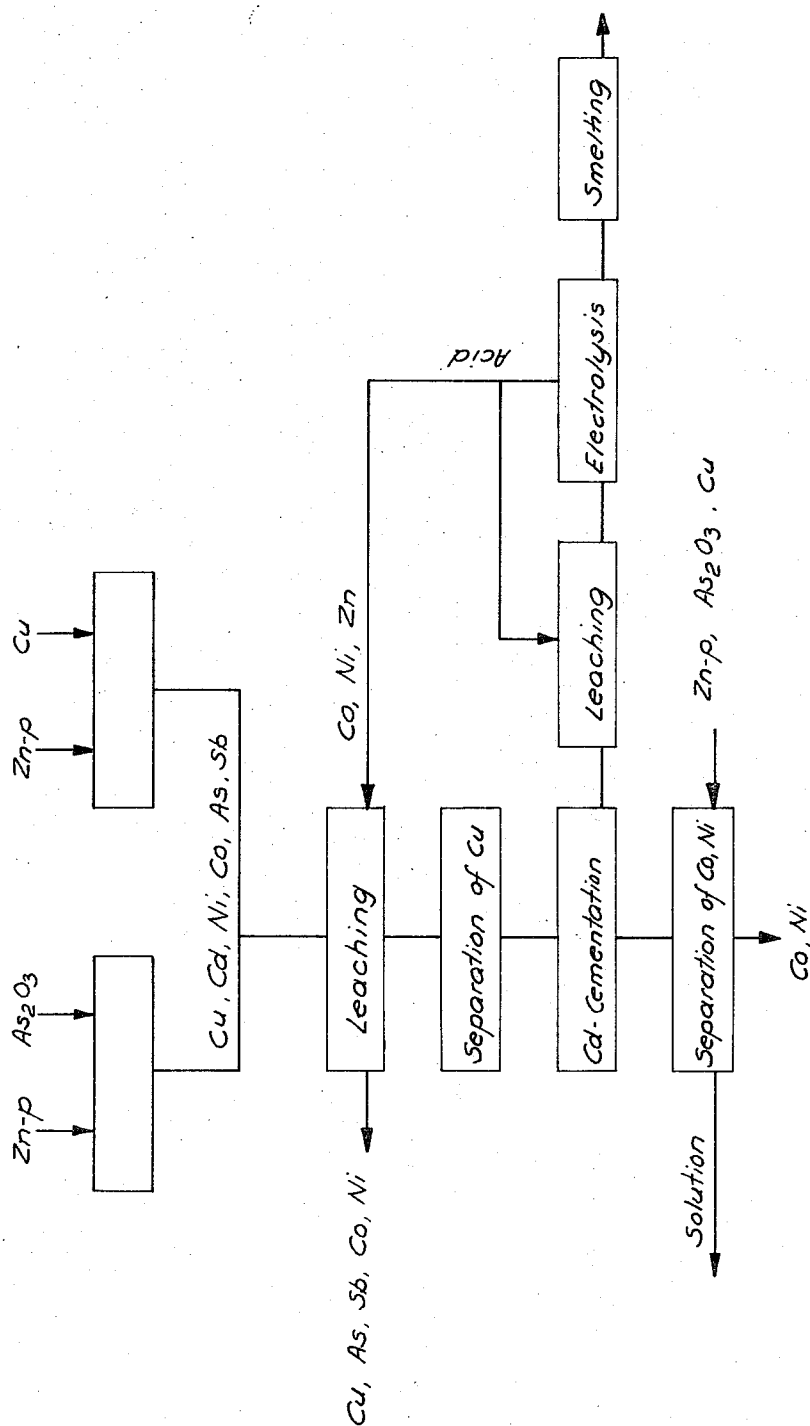
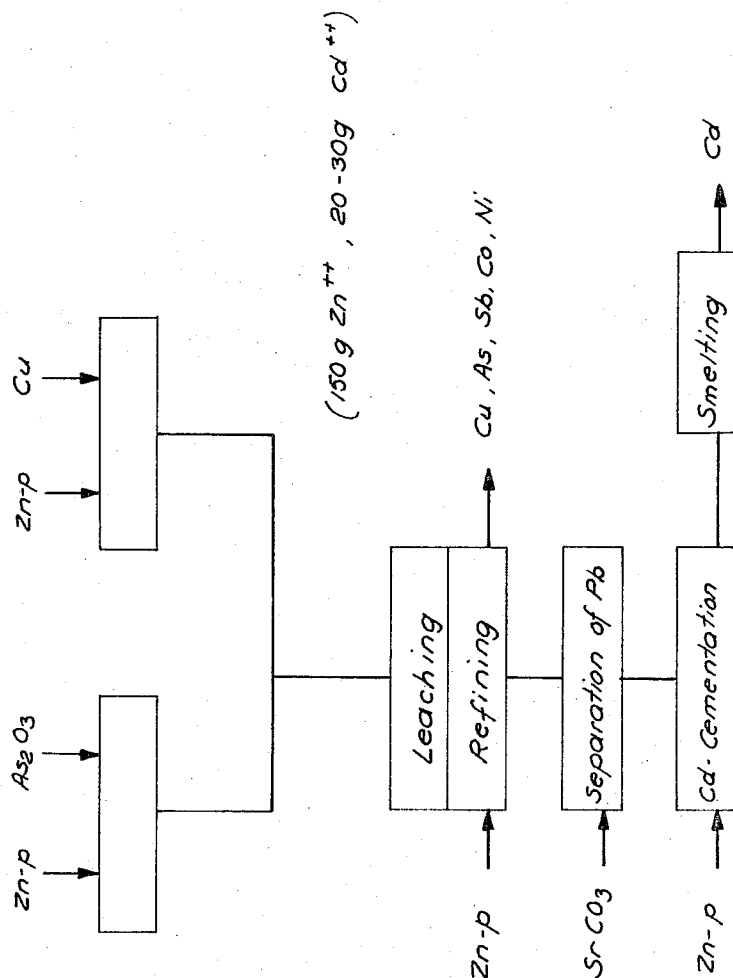


Fig. 4



PROCESS FOR PRODUCING CADMIUM

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to the field of producing cadmium and more specifically to a process for recovering cadmium by leaching a cementation precipitate from the refining of a solution from the Zn process.

2. Description of the Prior Art

Schematically, the zinc process is the following: ZnO, which has been obtained by roasting a material containing ZnS, is leached in the return acid from the electrolysis. The return acid contains H_2SO_4 and $ZnSO_4$ in varying proportions, depending on the circumstances prevailing in the electrolysis. The result of this leaching is a neutral $ZnSO_4$ solution containing impurities that have to be removed before the electrolysis. The refined solution is then conducted into the electrolysis process where Zn is separated and an equivalent amount of H_2SO_4 produced.

Some of the impurities present in the unrefined solution are of economic value, but most of them appear in such small quantities that their recovery is not economically profitable. Their withdrawal from the solution and the process is, however, very important; partly because they can precipitate with the zinc, the standards of purity of which are very high, and partly because they can complicate the electrolytic precipitation of zinc by lowering the overpotential of hydrogen at the cathode. The refining must also be very effective because the process solution circulates in a closed circuit, in which case substances that originally appear only in insignificant quantities can concentrate in the solution circuit.

The separation of iron is usually carried out by hydrolytic precipitation under oxidizing conditions, at which time part of the other substances — Ge, As, Sb — can be removed. After filtration, a solution is obtained from which Cu, Cd, and small quantities of Ni, Co, As, and Sb still must be removed. Of these, usually Cu and Cd are economically significant and are recovered, while the other substances are generally only removed from the process. The refining process of the solution must, therefore, be chosen taking into consideration adequate precipitation of the solution and a careful recovery of Cu and Cd.

Because all of the above substances are more noble than Zn, it is perhaps easiest to precipitate them with metallic zinc. This precipitation will remove all other substances except Co to such low contents as are required of an adequate refinement. However, Co is left if only Zn-powder is used, while an adequate precipitation is obtained by adding As or Sb compounds in the presence of a suitable amount of Cu. These added substances effect a slow precipitation of Cd, however, and a precipitated metal tends to oxidize very easily and redissolve.

In principle, there are, in this case, two economical processing choices for refining the solution if the solution contains cobalt.

1. Precipitation with pure Zn-powder during the first phase, and then removal of Co with a special reagent (usually α -nitroso- β -naphthole) during the second phase.

2. Precipitation during the first phase with Zn-powder + As (Sb) additive (if there is not enough of As (Sb)

in the solution), and, during the second phase, precipitation of the remaining Cd with pure Zn-powder.

Process 1 is very advantageous in regard to the recovery of Cd because all the Cd ends up in the Cd-circuit, which usually appears in connection with the refining of zinc, but it has some obvious disadvantages as well. Co will precipitate to some extent during the first phase and, therefore, follow Cd into the Cd-circuit. However, Co can be returned to the Zn-circuit which contains an outlet for Co. There must be an outlet for Ni in the Cd-circuit. However, this causes a remarkable inconvenience because Ni and Cd cannot be precipitated selectively enough with Zn-powder, and Cd, which precipitates first, tends to remain remarkably impure. Thus, an outlet for nickel and its simultaneous complete separation from cadmium cannot be obtained in a single Zn-powder precipitation. Therefore, process 1 cannot be considered satisfactory if, in addition to Co, Ni is present in the $ZnSO_4$ solution. On the contrary, process 2 offers a possibility of mutual outlet for the two substances. Furthermore, a Co content lower than 0.1 mg/1 can be obtained with process 2, which is difficult to achieve with α -nitroso- β -naphthole (FIG. 1).

When process 2 is used (see FIG. 2), advantage is usually taken of the above case in which Cd precipitates with great difficulty if As (Sb) is present. Therefore, the precipitation is carried out so that, during the first phase, the purpose is to keep Cd in the solution and to precipitate all the other substances more noble than Zn. Thus, an outlet into the Cu precipitate is created for all the impurities except Cd. The Cu precipitate then goes into the Cu smelting process, and a relatively pure Cd precipitate is obtained during the second phase. Impurities which, however, end up in small quantities in the Cd-circuit can be returned to the Zn-circuit before the refining of the solution; thus, and outlet in the Cd-circuit can be eliminated.

This method does have disadvantages; one of them being that a complete selectivity cannot be obtained in the precipitation. 10–15 percent of the Cd precipitates during the first phase while the Zn content of this precipitate is also considerable (20–30 percent). Both Cd and Zn in this Cu precipitate are virtual losses. Another disadvantage is that a completely pure Cd precipitate cannot be obtained either; small amounts of more noble metals as impurities cannot be avoided, and they require an outlet in the Cd-circuit or they must be returned to the Zn-circuit.

To decrease losses of Cd and Zn when using refining process No. 2, the refining could be carried out so that only a combined precipitate is produced and the entire amount of precipitated substances is treated in the Cd-circuit. While a more effective leaching of Cd and Zn is obtained, the Cd-circuit will contain all the impurities precipitated from the Zn-circuit. This, again, means that their outlet in the process must be in the Cd-circuit, and that returning to the Zn-circuit cannot be used as the only refining process in the Cd-circuit. Also, because the amount of impurities is considerably high, the refining processes must be such that the losses of Cu, Cd, and Zn are small, and sufficiently effective to produce pure Cd in a relatively simple manner.

If the combined precipitate is leached in the return acid from the Zn-electrolysis, a rather complete leaching of Zn, Cd, Ni, and Co is obtained, while Cu and As do not dissolve. If air is present Cu and As also begin to oxidize and dissolve after Zn and Cd have dissolved.

For this reason the Cu^{++} concentration in the solution can be used to indicate the completion of the leaching.

After the leaching, the process can be continued in the following manner which is being used or has been used (see FIG. 3, Alf, A. J.: Journal of Metals, Sept. 1958, pp. 607-610). The leach residue is filtered out of the solution and Cu^{++} precipitated from the refined solution with Zn-powder. Cd is filtered out of the solution, and Co and Ni are precipitated in the ordinary manner from the solution that has a low Cd content, with Zn-powder and As (Sb) + Cu additive. After this process, the refined solution can be returned to the Zn-circuit after a filtration.

In this manner, an acceptable outlet for Co and Ni is obtained in the sense that losses of Cd and Zn remain small. When Cd is precipitated with Zn-powder from an impure solution such as the above, Ni, in particular, and, to some extent, Co tend to precipitate and so contaminate the precipitated Cd. Therefore, additional measures are required to remove these two elements and Zn, which is used in excessive amounts in the precipitation process. The most common method is to leach a Cd sponge in H_2SO_4 (return acid from Cd-electrolysis) and to then precipitate Cd electrolytically, in which case, Co and Ni will not precipitate to any noteworthy extent. Because the contents of these elements and Zn gradually increase in the electrolyte, they are partly returned to the leaching process of the cementation precipitate produced by the coherer. The electrolysis, which is usually carried out with Pb-Ag anodes, has the disadvantage of the Pb content at the cathode growing quite high (0.01 - 0.015 percent); in addition, almost the same amount of Zn is obtained as an impurity. The cathodes are then smelted in alkali smelt, at which time Zn oxidizes and dissolves as a zincate into the slag; while an equally effective refinement is not obtained in regard to Pb.

SUMMARY OF THE INVENTION

According to the invention all the dissolved impurities but Pb are removed from the solution by cementing them with a suitable reducing agent, such as Zn metal, whereafter Sr or Ba salts are added to the filtered solution to precipitate the Pb. Cd is cemented and separated from the solution and smelt refined with alkali to remove Zn.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 and 2 show the flow diagram of processes 1 and 2, respectively,

FIG. 3 shows a flow diagram of how the process may be continued after the leaching, and

FIG. 4 shows a flow diagram of a preferred embodiment of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

After the leaching of the cementation precipitate, all the metals more noble than Cd are removed from the solution before the precipitation of Cd. At this time a Cd sponge is obtained in which the only impurity is Zn. The Zn can be easily removed with alkali smelt refining process. It is possible to carry out the process when Co and Ni (as well as Cu, As, Sb) are removed from the CdSO_4 solution before the cementation of the Cd sponge as explained below (see FIG. 4.).

After the leaching of the Cd and Zn contained in the combined cementation precipitate obtained from the refining process of the solution from the Zn-circuit (refining of the solution takes place according to process 2), when Co and Ni are also present in the solution, the insoluble Cu-As precipitate is left in the solution and the temperature is raised (most advantageously above 90°C). An amount of Zn corresponding to the Cu which may have dissolved is first added; then Zn is added in portions until Co has been removed. This proves that Cu, Ni, As, and Sb have also been removed from the solution. In this case the As and Cu required for the refining of the Zn-circuit are reused, and, in addition, they are used so that Cd, in spite of its high content, remains in the solution.

This refining has removed all the substances that are more noble than Cd, except Pb, so completely that their contents in the Cd sponge are small enough to make additional refining for their removal absolutely unnecessary. Pb is the only impurity which will be present in the Cd sponge and which cannot be effectively removed by alkali smelting. Pb can be precipitated from an acidic sulphate solution as an isomorphic Sr-Pb-sulphate by adding SrCO_3 (Ba can also be used) (U.S. Pat. No. 2,496,996). In this case, such a low Pb content as 0.1 mg/l can be obtained in the solution giving a maximum content of 5 ppm. in the cadmium sponge if the Cd content in the solution is 20 g/l.

After Pb has been removed, the Cd is precipitated with a high-class Zn-powder, in which case the amount of precious impurities is determined by their content in the Zn-powder. Zn and a number of other unprecious elements, such as Fe, Si, Al, Mn, and Mg are then removed simply by alkali smelt refining.

In this process, Cd with a degree of purity of at least 99.995 percent can be obtained in a simple manner from such a difficult material as that obtained from solution refining according to process 2.

An outlet for Co, Ni, Cu, As and Sb and, at the same time their complete removal can be obtained in the Cd-circuit with this process. In this case the remainder of the Cd production process will be simple because these elements need no longer be taken into consideration.

The extraction of Cd and Zn will also be most satisfactory: firstly, because all the elements, As, Co, and Ni, which greatly increase the dissolving rate of Cd and Zn by lowering the overpotential of hydrogen, are present in higher proportions. Secondly, the proportions of these impurities in the solution need not be taken into consideration because the following refining process will effectively reprecipitate them. The leaching can therefore be carried out with the best possible leaching rate of Cd and Zn.

EXAMPLE I (LAB SCALE)

Cementation precipitate with the following composition was used as raw material:

Zn %	Cd %	Cu %	As %	Co %	Ni %
37.7	9.8	16	2.4	0.04	0.03

After leaching with return acid from Zn process (60 g Zn and 180 g H_2SO_4 /l) at the temperature of 70°C , the following solution was obtained:

Cd g/l	Cu g/l	As mg/l	Co mg/l	Ni mg/l
22.5	4.3	82.5	105	105

After 4.9 g Zn-powder/l was added (=equivalent amount per Cu⁺⁺ (ZnO = 10 percent) + 1.95 g Zn-powder/l at the temperature of 90°C, the following solution was obtained:

Cd g/l	Cu mg/l	As mg/l	Co mg/l	Ni mg/l	Pb mg/l
22.5	0.2	0.10	1.6	<0.5	7.4

3 × 0.3 g SrCO₃/l was added to the solution at half-hour intervals and, after this, the solution contained 0.05 mg Pb/l. From this solution was obtained a Cd sponge with the following composition (the Zn-powder used in the cementation process contained 30 ppm Pb):

Zn %	Pb %	Cu %	Fe %	Si %	Mn %	In %	Mg %	Ag %
2.5	0.002	0.002	0.008	0.007	0.0002	0.0005	0.0003	0.0003

Co and Ni were not observed, which means that their content was less than 3 ppm.
This Cd sponge was smelted in NaOH leaving as impurities the following:

Zn %	Pb %	Cu %	Fe %	Ag %
<0.001	0.0015	0.001	0.0007	0.0003

EXAMPLE II (TECHNICAL SCALE)

Rawmaterial: combined Cu- and Cd-cake						
Zn %	Cd %	Cu %	As %	Sb %	Co %	Ni %
51.2	11.1	15.7	2.7	0.3	0.04	0.05

The cake was leached with return acid from Zn-electrolysis for about 12 hours at an acid concentration of 3 – 10 g H₂SO₄/l. Solution and leach residue showed the following analysis:

Solution						
Cd g/l	Cu mg/l	As mg/l	Sb mg/l	Ni mg/l	Co mg/l	H ₂ SO ₄ g/l
18.4	240	24.2	3.1	122	83	3.2
Residue						
Cu %	Cd %	Zn %				
61.5	0.27	1.3				

Zn-dust was added to the suspension until pH reached 5. Zn-dust consumption was 2.6 g/l. Temperature was above 90°C. As Co-spot test showed Co < 2 mg/l the suspension was filtered.

Analysis of solution:						
Cd	Cu	As	Sb	Ni	Co	Pb

-Continued

g/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
18.1	0.3	0.3	<0.1	0.2	0.6	3.7
Analysis of residue:						
Cu %	Zn %	Cd %				
64.3	1.2	0.8				

BaCO₃ was then added to the solution as a water-slurry. Amount of BaCO₃ added was 1 g/l and added during 2 hours. In the beginning was also 0.3 g Zn dust/l added. Solution was then filtered.

Analysis of solution:

Cu mg/l	Co mg/l	Ni mg/l	Pb mg/l	As mg/l	Sb mg/l
<0.1	0.6	0.2	<0.1	<0.1	<0.1

Cd-sponge was cemented from this solution with a Zn-dust containing:

Cu ppm	Pb ppm
2.4	8.6

The analysis of the sponge was as follows:

Zn %	Cu ppm	Pb ppm	Fe ppm	Ni ppm	Sn ppm	Sb ppm	In ppm	Si ppm	Mn ppm	Mg ppm	Ag ppm
0.77	7	8	15	5	<3	<10	10	5	30	30	3

The sponge was briquetted and the briquettes put in an electrically heated iron pot supplied with a stirrer. The briquettes were covered with NaOH and heated until all was melt. Agitator was started and agitation continued during 2 hours.

The metal showed then the following analysis:

Zn ppm	Cu ppm	Pb ppm	Fe ppm	Ni ppm	Ag ppm
4	7	9	6	6	3

What is claimed is:

1. A method for facilitating recovery of cadmium from a cadmium sulfate solution derived from an electrolytic zinc process comprising (a) adding a reducing agent to a cadmium sulfate solution containing in solution the following impurities: lead and at least one metal selected from the group consisting of cobalt and nickel, and at least one metal selected from the group consisting of cooper, zinc, arsenic, and antimony, and containing undissolved copper and arsenic or undissolved copper, arsenic, and antimony, to cement substantially all dissovded metal, (b) filtering the solution to remove the cemented metal impurities except lead and undissolved copper and arsenic or copper, arsenic, and anitmony, and (c) adding a salt of at least one metal selected from the group consisting of strontium and bar-

ium to the filtrate to remove the lead, thereby producing pure cadmium solution.

2. The method of claim 1 wherein the reducing agent is zinc.

3. The method of claim 1 wherein the cadmium sulfate solution contains dissolved nickel, copper, lead and zinc, and undissolved dispersed copper and arsenic.

4. The method of claim 1 further comprising, after adding said salt, cementing cadmium from the solution, separating the cemented cadmium from the solution, and smelt refining the separated cadmium with alkali.

5. The method of claim 4 wherein the cementing agent for cadmium is zinc, the cemented cadmium and zinc are leached in an acid medium, and then electrolyzed, and acid from the electrolysis is recycled to the leaching step.

6. The method of claim 4 wherein the cadmium sulfate solution contains dissolved nickel, copper, lead and zinc, and undissolved dispersed copper and arsenic.

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