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- (71) Applicant (for all designated States except US): **OUTOKUMPU TECHNOLOGY OY** [FI/FI]; Riihitontuntie 7, FI-02200 Espoo (FI).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **LEHTINEN, Leena** [FI/FI]; Maaherrankatu 25 B 20, FI-28100 Pori (FI). **OINONEN, Yrjö** [FI/FI]; Pyynkuja 6, FI-67800 Kokkola (FI).
- (74) Agent: **OUTOKUMPU TECHNOLOGY OY, IPR MANAGEMENT**; P.O. Box 86, FI-02201 Espoo (FI).
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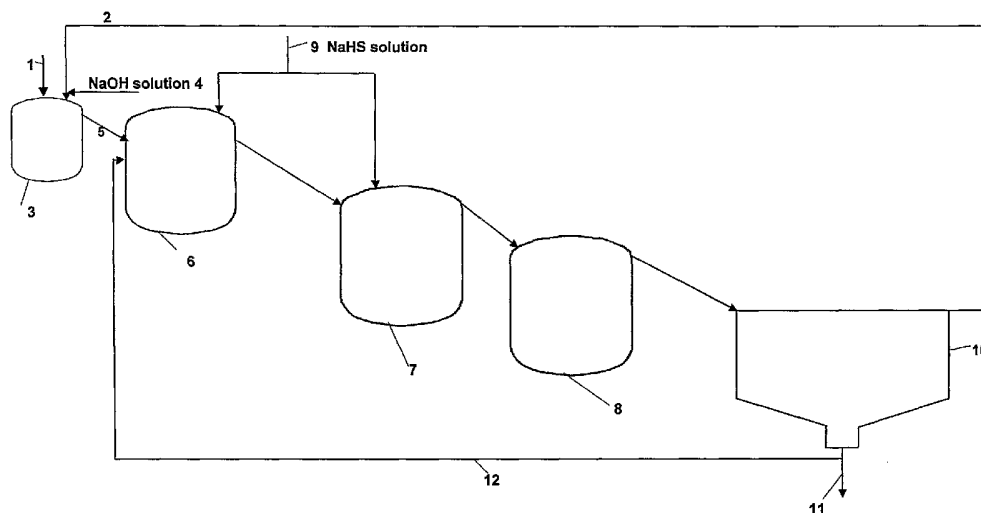
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[Continued on next page]

(54) Title: METHOD FOR TREATING IRON RESIDUE



(57) Abstract: The invention relates to a method whereby iron residue generated in the hydrometallurgical production of zinc is neutralised and sulphidised in order to stabilise the harmful metals remaining in said residue. The conversion of harmful metals into their sulphides is carried out after neutralisation with a sulphide solution in at least one reactor, whereby the oxidation-reduction potential is adjusted to be in the negative range and preferably between -100 and -250 mV vs. Ag/AgCl electrode and the pH to a range between 7.5-9. The stability of the sulphides is improved by recirculating the residue within the sulphidation stage. The amount of sulphide solution feed is 1.5 - 2.5 times as much as the equivalent amount required by the sulphidation reactions. The water is removed from the waste residue formed in an economic way.



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METHOD FOR TREATING IRON RESIDUE

FIELD OF THE INVENTION

The invention relates to the treatment of the dischargeable iron residue that
5 is generated in the hydrometallurgical production of zinc, so that the other
metals contained in the residue are in stable form.

BACKGROUND OF THE INVENTION

The final treatment stage of the iron residue generated in the
10 hydrometallurgical production of zinc is generally filtration. The zinc content
of the solution to be removed from the residue in filtration is high, and for that
reason the solution is routed to neutral leaching and from there via solution
purification to zinc fabrication. Iron residue is classified as hazardous waste,
which is kept at the waste site. Usually the iron residue is either jarosite or
15 goethite, less commonly hematite. The solid content of the iron residue
depends to some extent on the treatment method. It is important from the
environmental aspect that the concentrations and amounts of hazardous
substances in the iron residue are as small as possible. Harmful metals left
in the residue are usually in the moisture remaining in the residue, in other
20 words due to poor washing and/or filtration of the residue. The most
important metals that end up in the waste site are cadmium and zinc, and
arsenic and mercury may also be present.

Most zinc producers route the iron residue formed directly to the waste site
25 after filtration, without removing the harmful substances in it, since obviously,
the aim is to treat waste at the lowest possible cost. However, it is quite likely
that in the future a more thorough recovery or stabilisation of harmful
substances will be required before iron residue can be transferred to a waste
site. Some zinc manufacturers neutralise iron residue, whereby soluble
30 metals are obtained in the residue as hydroxides.

To keep the amount of waste small, the residue should be made as dry as possible. According to one quality assurance test, the maximum liquid/solid (L/S) ratio in residue to be routed to a waste site should be 2, which corresponds for instance to a moisture content of 67% for jarosite slurry.

5

One iron residue stabilisation method is cementation. When cement is added to jarosite in the proportion of 10-30% of the amount of jarosite, the harmful metals present in the jarosite are then bound in insoluble form. At the same time, the jarosite is hardened, which prevents dusting and decomposition.

10 The method requires that the iron be precipitated as sodium jarosite, because when ammonium jarosite is stabilised, malodorous ammonia is formed. Cementation in itself is a good stabilisation method, but it increases the overall amount of waste by an amount equivalent to the amount of cement, and the aim is to keep the amount of waste as small as possible.

15

PURPOSE OF THE INVENTION

The purpose of the method according to the invention is to obtain iron residue generated during the hydrometallurgical production of zinc, in which the harmful metals contained in the residue are treated so as to remain
20 stable even in variable conditions and in which stabilisation does not increase the amount of waste. The iron residue is stabilised by sulphidation. It has been shown that in some conditions the hydroxides of harmful metals are not enough slightly soluble. Moisture is removed from the residue so that the residue is easy to store.

25

SUMMARY OF THE INVENTION

The invention relates to a method whereby iron residue generated in the hydrometallurgical fabrication of zinc is neutralised and sulphidised in order to stabilise the harmful metals remaining in said residue. The conversion of
30 harmful metals into their sulphides is carried out after neutralisation with a sulphide solution in at least one reactor, whereby the oxidation-reduction

potential is adjusted to be in the negative range and preferably between -100 and -250 mV vs. Ag/AgCl electrode and the pH to a range between 7.5 – 9.

According to one preferred embodiment of the invention, the oxidation-
5 reduction potential is regulated to be in the range of -200 - -250 mV vs. Ag/AgCl electrode at least in one reactor.

According to another preferred embodiment of the invention, the stability of the sulphides is improved by recirculating the residue within the sulphidation
10 stage.

According to another preferred embodiment of the invention, an amount of sulphide solution is fed which is equivalent to 1.5 – 2.5 times the amount of metal to be precipitated.

15 Water is removed from the waste residue generated in an economic manner.

The essential features of the invention will be made apparent in the attached claims.

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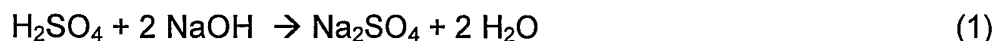
LIST OF DRAWINGS

Figure 1 presents the flow chart of the stabilisation and thickening of the waste residue.

25 DETAILED DESCRIPTION OF THE INVENTION

When it is desired to obtain the other metals contained in the iron residue generated in the hydrometallurgical production of zinc in a stable, environmentally friendly form and to neutralise the acid in the moisture, it should be done using the cheapest possible additives since it is a question of
30 waste processing. Iron residue, which is at least one of the following: jarosite, goethite or hematite, is neutralised with alkali hydroxide or earth alkali hydroxide such as NaOH or Ca(OH)₂, so that the acid contained in the

moisture of the residue is neutralised and the metals are precipitated as their hydroxide:

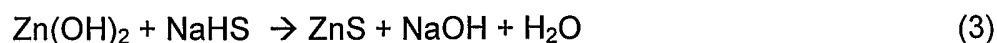


Calcium hydroxide is a cheap neutralising and precipitating agent, but it causes technical problems and the amount of residue increases.

10

Hydroxides of harmful metals are fairly stable compounds, but since in some conditions hydroxides also dissolve, it is more environment-friendly to get the metals in an even more stable form. This can be achieved by sulphidising the generated hydroxides. Some sulphide solution can be used for sulphidation, for example the low-cost sulphide-lye solution generated as a by-product in the wood processing or some other industry, of which the main constituent is sodium hydrogen sulphide NaHS. A little sodium sulphide Na₂S may also be present. As a consequence of sulphidation the harmful metal contained in the iron residue are made to react and form sulphides, which are very stable in storage conditions. The following reactions occur during sulphidation, which are presented here with regard to zinc, but also apply to cadmium and other harmful metals:

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20
25



The method according to the invention is illustrated by the flow chart attached in Figure 1. Before stabilisation the untreated iron residue is filtered and the solution from filtration is routed to the actual zinc process circulation. The filter-dry iron residue 1 is slurried during stabilisation in the stabilisation circuit by means of aqueous solution 2. After slurring, the moisture content of the residue is in the region of 80-85%, i.e. the solids content is around 350

30

– 450 g/l. Once the other metals contained in the iron residue are stabilised, the residue is neutralised in the first stage in a neutralisation reactor 3 with lye solution 4. The pH of the slurry is raised in neutralisation by means of lye to a value of 7-8, so that the jarosite is stable. If the pH is higher than 9, jarosite has a tendency to decompose partially in the sulphidation treatment that follows neutralisation. If on the other hand the pH is much lower, the sulphide solution used in sulphidation starts to decompose and form hydrogen sulphide, which is undesirable for reasons of occupational hygiene.

10 The neutralised residue 5 is routed on to sulphide solution treatment (NaHS) in order to convert the metal hydroxides into the corresponding sulphides. The slurry exiting the neutralisation stage is routed from the neutralisation reactor 3 as overflow to the sulphidation stage, which may take place in one or several reactors. The sulphidation shown in the diagram has three
15 reactors 6, 7 and 8, but in applications according to the invention, the number may be smaller or larger. When several reactors are used it is preferable to feed the sulphide solution 9 into several reactors. According to the diagram, the feed takes place into the first two reactors. All the reactors are equipped with a mixer to achieve even mixing of the reagent throughout
20 the entire volume of the reactor (not shown in detail).

The sulphide solution feed into the reactors is adjusted by means of the oxidation-reduction potential and the pH, so that the pH is adjusted in the region of 7.5 – 9 and the redox potential preferably in the region of -100 - -
25 250 mV vs. Ag/AgCl electrode. A Pt electrode is used as measurement electrode. It is beneficial that the redox potential is kept in the range of -200 - -250 mV in at least one of the reactors. A low redox potential achieves the sulphidation of the metals in the slurry. The required pH adjustment is performed by means of alkali hydroxide or earth alkali hydroxide, preferably
30 the same hydroxide used in neutralisation (not shown in detail). The sulphidation of harmful metals binds the metals to the solid matter and the

amount of soluble metal remaining is below the limits set by the environmental authorities.

The iron residue slurry is routed from one reactor to another as overflow and
5 from the final reactor to solids separation, as shown in the flow chart. The
stability of the sulphides that are generated is promoted by circulating the
residue from the solids and solution separation stage to sulphidation,
preferably to the first reactor. Recirculation achieves the coarsening of the
sulphides generated, which in turn makes it more difficult for them to
10 dissolve. For example, in the case of cadmium a lesser degree of solubility is
achieved when the residue is recirculated. The amount to be recirculated is
preferably 20 – 70% of the residue exiting solids separation. Recirculation
alone is not sufficient, however, and the feed of sulphide solution should be
specified to occur in the region described above, particularly by means of
15 redox potential regulation.

It has been found that sulphidation reactions proceed beneficially if the
amount of sulphide solution fed is 1.5 – 2.5 times more than the equivalent
amount needed in the sulphidation reactions (3)-(4) of harmful metals.

20

The sulphidation time should not be too long, for instance over 5 h, since too
long a delay results in the oxidation of the sulphide solution into thiosulphate.
The sulphidation time is in the region of 2-5 h, preferably 3h. The formation
of thiosulphate in turn results in a fall in pH, which means that the fine-
25 grained sulphides start to decompose.

Regarding environmental factors and the effective use of the waste site, it is
beneficial that the iron residue is brought to the waste site as dry as possible.
The preferred moisture content is around 30-50%, i.e. the solids content of
30 the residue is over 750g/kg. Dry residue can be taken directly to the desired
site and compressed there. In this way the residue is fit for use directly in the

making of various structures and can be landscaped as the construction of the waste site proceeds.

If sulphidised iron residue is pumped as slurry to the waste site, settling ponds must first be built there, which are equipped with irrigation ditches, along which the water separated from the residue can be conveyed back to the process. In this way the iron residue dries and can be later transferred to its final storage site.

One alternative for reducing the moisture of the iron residue is to perform neutralisation and sulphidation at a high slurry density, whereby the problems related to water removal can be at least partially eliminated. A high slurry density requires however special mixers, which entails extra costs in comparison with normal mixers. In addition, raised viscosity has a noticeable effect on the pH and potential measurements required by the process. When sulphidation is performed with a high solids content, fluctuating solids contents can easily be generated locally in the reactors. If the pH rises locally too high, it causes the decomposition of the iron residue and its reaction into sulphide, which in turn consumes sulphide solution.

It is beneficial to neutralise and sulphidise iron residue at a relatively low solids content and to perform solids separation after sulphidation in order to raise the solids content of the waste. One preferred alternative for solids separation is the thickening of the sulphidised iron residue. According to Figure 1, the waste residue with high fluid content that exits the sulphidation stage is routed to a thickener 10, and its overflow 2 is recirculated to the slurring of stabilising residue. Since the overflow is recirculated, it does not need to be clear, and may contain fine-grained sulphides, which coarsen in recirculation. At the same time any possible metals still dissolved in the solution overflow are recirculated to neutralisation and sulphidation and precipitate out. Of the waste residue 11 obtained as the thickener underflow, some 12 is circulated back at least to the first sulphidation reactor in order to

coarsen the sulphides and form nuclei for the sulphides. The solids content of the residue is raised preferably to the region of at least 700 g/l. One preferred thickener type is the paste thickener, with which an even higher solids content can be achieved than a conventional thickener.

5

Another alternative way to raise the solids content of iron residue is a centrifuge. The centrifuge overflow and underflow are recirculated in the same way as described above.

- 10 Yet another alternative method for raising the solids content of iron residue is filtration. Filtered residue is suitable for landscaping directly, but acquisition of filtration equipment is quite an expensive investment for waste processing.

EXAMPLES

15 Example 1

The stabilisation of harmful metals in iron residue was studied in pilot-scale test. Equipment was used in the test comprising four reactors, of which the first was a neutralisation reactor NR and the three following were sulphidation reactors SR1, SR2 and SR3. Each reactor was equipped with a
20 blade mixer. The size of the NR reactor was 5.5 l, SR1 was 14 l, and SR2 and SR3 17 l. pH adjustment was used in the neutralisation reactor, potential adjustment and pH measurement in the first two sulphidation reactors, and potential measurement and pH measurement in the final reactor. The measuring electrode in potential measurement was a Pt electrode and the
25 reference electrode was an Ag/AgCl electrode. The sulphidation time was 3h.

The iron residue used in the tests was filter-dry jarosite residue, which was slurried in the neutralisation reactor to a slurry density of about 400 g/l. The
30 soluble zinc content of the residue was in the range of 0.2 – 0.3%, which corresponds to 3.4 – 3.9 g/l and the cadmium content was around 75 mg/l.

The amount of lye, NaOH, fed into the jarosite slurry was adjusted using pH to a value of 7.5.

5 The jarosite residue was routed from the neutralisation reactor as the overflow into the first sulphidation reactor. The NaHS content of the sulphide solution used for sulphidation was around 90 g/l and the Na₂S content around 4 g/l. The sulphide solution was fed into the first two reactors so that the potential of the first reactor SR1 was adjusted to be between -100 - -150 mV with a pH of 8.3 – 8.5, and the potential of the second reactor SR2 was
10 between -200 - -250 mV with a pH of 7.9-8.7. The sulphide solution feed was 1.5 – 2.5 times as much as the equivalent amount of harmful substances. No sulphide solution was fed into the last reactor SR3 and its potential was between -100 - -150 mV and the pH between 7.7 – 8.6.

15 After three hours of sulphidation the amount of soluble zinc was around 0.5 mg/l and the amount of cadmium was around 0.01 mg/l.

The recirculation of the residue was also investigated in these tests, in this case from reactor SR3 to reactor SR1. It was found that residue recirculation
20 improves the sulphidation of cadmium. For example, it was discovered in subsequent residue solubility tests that when the recirculated amount was 40% of the SR3 reactor overflow, the amount of both zinc and cadmium soluble compounds fell to a tenth in comparison with sulphidation without recirculation. When the residue is routed from the final reactor to solids
25 separation, obviously the residue to be recirculated is taken from the solids separation underflow.

PATENT CLAIMS

1. A method to stabilise the harmful metals in the iron residue generated in the hydrometallurgical production of zinc, whereby the iron residue is slurried, the acid in the residue is neutralised and the harmful metals are made to react into their oxides by means of alkali hydroxide or earth alkali hydroxide, **characterised in that** the metal oxides in the iron residue are further converted into sulphides principally by means of a solution containing sodium hydrogen sulphide, whereby the oxidation-reduction potential of the solution is adjusted to be in the negative zone and the pH between 7.5 – 9.
2. A method according to claim 1, **characterised in that** the oxidation-reduction potential is adjusted to the region of -100 - -250 mV vs. Ag/AgCl-electrode.
3. A method according to claim 1 or 2, **characterised in that** the iron residue is at least one out of jarosite, goethite and hematite.
4. A method according to any of preceding claims 1-3, **characterised in that** the harmful metals are at least zinc and cadmium.
5. A method according to any of preceding claims 1-4, **characterised in that** the pH of the slurry is raised to a value of 7-8 in the neutralization stage.
6. A method according to any of preceding claims 1-5, **characterised in that** the alkali hydroxide used for neutralization is sodium hydroxide.
7. A method according to any of preceding claims 1-6, **characterised in that** sulphidation is carried out in several reactors.

- 5
8. A method according to claim 7, **characterised in that** the oxidation-reduction potential of at least one reactor is adjusted by means of sulphide solution to the range -200 - -250 mV vs. Ag/AgCl electrode.
- 10
9. A method according to any of preceding claims 1-8, **characterised in that** the sulphide solution feed is 1-5 – 2-5 times as much as the equivalent amount required for the sulphidation reactions of the harmful metals
- 15
10. A method according to any of preceding claims 1-9, **characterised in that** the pH adjustment of sulphidation is carried out by means of alkali hydroxide or earth alkali hydroxide.
- 20
11. A method according to any of preceding claims 1-10, **characterised in that** after sulphide precipitation the residue is routed to solids separation.
- 25
12. A method according to claim 11, **characterised in that** the underflow from solids separation is circulated back to the sulphidation stage.
- 30
13. A method according to claim 12, **characterised in that** the amount of residue to be recirculated is 20 – 70% of the solids separation underflow.
14. A method according to claim 11, **characterised in that** the overflow of solids separation is routed to iron residue slurring.
15. A method according to claim 11, **characterised in that** solids separation of the sulphidised iron residue is performed by thickening.

16. A method according to claim 15, **characterised in that** the thickener used in thickening is a paste thickener.

5 17. A method according to claim 11, **characterised in that** solids separation of the sulphidised iron residue is performed by centrifuging.

10 18. A method according to claim 11, **characterised in that** solids separation of the sulphidised iron residue is performed by filtration.

19. A method according to any of preceding claims 1-18, **characterised in that** the sulphide precipitation time is between 2-5 h and preferably 3h.

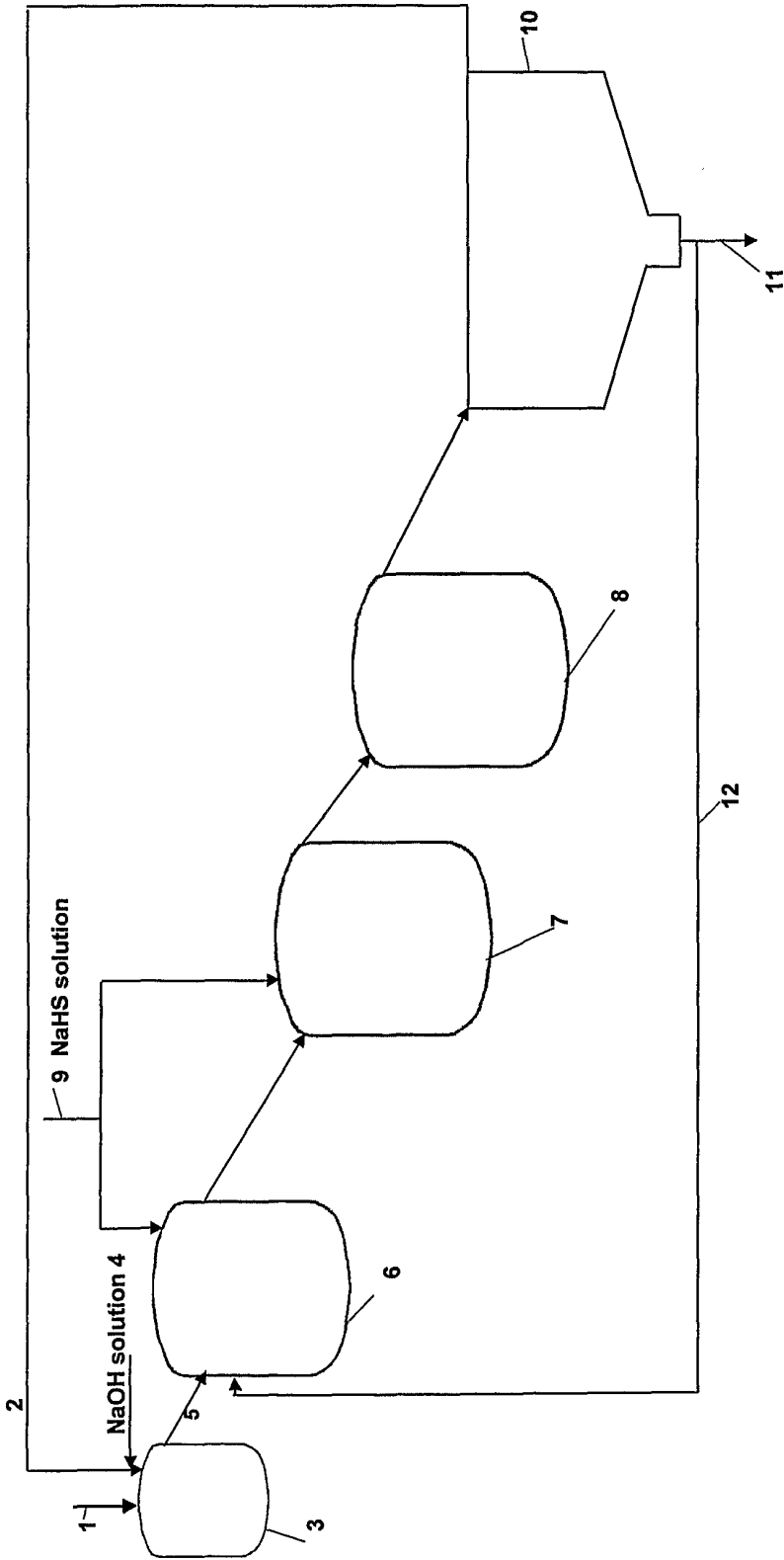


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2005/000360

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: A62D, B09B, C22B, C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	DATABASE EPODOC/EPO abstract & JP 20 02316123 A (DOWA MINING CO) 29 October 2002 (2002-10-29) --	1-19
A	DE 3800616 A1 (BOGUSLAWSKI, ZBIGNIEW, DR.), 20 July 1989 (20.07.1989), page 7, line 1 - line 31, abstract ---	1-19

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

20 December 2005

Date of mailing of the international search report

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Name and mailing address of the ISA/
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Authorized officer

Mårten Hulthén/Els
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2005/000360

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	DATABASE EPODOC/EPO abstract & JP 57 094383 A (BABCOCK HITACHI KK) 11 June 1982 (1982-06-11) --	1-19
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INTERNATIONAL SEARCH REPORT
Information on patent family members

26/11/2005

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