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(54) Titre : PROCEDE POUR SEPARER DES MATERIAUX CONTENANT DU SULFURE A L'AIDE DU PEROXYDE D'HYDROGENE

(54) Title: PROCESS FOR SEPARATING SULPHIDE-CONTAINING MATERIALS USING HYDROGEN PEROXIDE

(57) Abrégé/Abstract:
The invention relates to a process for separating sulphide-containing materials using hydrogen peroxide. Within the meaning of the invention, sulphide-containing materials are those of natural origin, e.g. mono or polysulphide ores, or products of industrial processes, e.g. mining spoil or products of metal smelting.

**PCT**

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**(54) Title:** PROCESS FOR SEPARATING SULPHIDE-CONTAINING MATERIALS USING HYDROGEN PEROXIDE

**(54) Bezeichnung:** VERFAHREN ZUR AUFTRENNUNG SULFIDHALTIGER MATERIALIEN UNTER VERWENDUNG VON WASSERSTOFFPEROXID

**(57) Abstract**

The invention relates to a process for separating sulphide-containing materials using hydrogen peroxide. Within the meaning of the invention, sulphide-containing materials are those of natural origin, e.g. mono or polysulphide ores, or products of industrial processes, e.g. mining spoil or products of metal smelting.

**(57) Zusammenfassung**

Die Erfindung betrifft ein Verfahren zur Auftrennung sulfidhaltiger Materialien unter Verwendung von Wasserstoffperoxid. Als sulfidhaltige Materialien sind im Sinne der Erfindung Materialien natürlichen Ursprungs, wie z.B. mono- oder polysulfidische Erze, oder Produkte industrieller Prozesse, wie z.B. Restprodukte des Bergbaus und der Metallerzeugung zu verstehen.

# A Process for the Separation of Materials Containing Sulfides

The invention relates to a process for separating sulfidic materials, using hydrogen peroxide. In the meaning of the invention, sulfidic materials are understood to be materials of natural origin, such as mono- or polysulfidic ores, or products from industrial processes, such as residual products from mining and metal manufacturing.

Thus, residual products from nonferrous metal smelting, particularly copper slate smelting, represent a considerable environmental risk as a result of their high content of heavy metals, toxic organic components, and radionuclides. The so-called Theisen sludge which is a residual product from the Mansfeld copper slate smelting in Saxony-Anhalt, Germany, may be mentioned as a representative example. Similar residues from nonferrous metal production also arise at other locations at home and abroad.

Said Theisen sludge is a fine-grain solids mixture, consisting essentially of sulfides and sulfates of the metals copper, lead and zinc, with the zinc phases prevailing. The average contents of these metals are around 1.2% for copper, 14% for lead, and 18% for zinc.

As has been shown by investigations related to the morphology and structure of its sulfides, Theisen sludge is a mixture of primary mineral phases of ore and secondary processing products. It represents a "solid solution" of particles having an average grain size of 1.25 $\mu$m, these particles themselves being aggregates of even smaller parti-

cles (<1 μm).

It is well-known from the literature that current technologies of metal recovery cannot be used on this material (cf., Leipner et al., Technisch-wissenschaftliche Betrachtungen zur Verarbeitung von Mansfelder Theissenschlamm (Flugstaub) - Erzmetall 44/11, 560-565; Weinheim (1991); Lorenz et al., Theisenschlämme im Mansfelder Revier, Verwertung oder Deponierung - Ein Konzeptvorschlag zur Verwertung, Metall 46/9, 955-957; Frankfurt/Main (1992)). Owing to the fact that from an environmental viewpoint, the suggested pyrometallurgical treatment processes practiced previously here and there are no longer acceptable today, the Theisen sludges are dumped into landfills.

However, not only Theisen sludges represent an environmental risk but rather, sulfidic materials altogether are a source of environmental pollution. Namely, they are subject to slow oxidation under ambient conditions, thereby liberating sulfuric seep waters and heavy metals which pollute soils, groundwaters and surface waters.

On the other hand, sulfidic materials of natural origin, such as polysulfide ores, not only consist of lead, zinc, copper, and iron sulfides but rather, the sulfidic ore minerals may also include noble metals such as gold and/or silver, the content of these noble metals being highly variable, depending on the particular ore. Even the residues from the flotation of polysulfide ores, essentially iron sulfides, may still contain a percentage of gold and/or silver. Even today, $FeS_2$ is used in the production of sulfuric acid in those countries where pyrite is abundant, while these residues are dumped as waste in all the other countries.

In addition, naturally occurring pyrites

(monosulfidic ores) may also contain a low percentage of noble metals, which might be interesting in economic terms.

Therefore, it was the object of the invention to develop a process for separating sulfidic materials, which is favorable in cost and permits both separating the metals contained and minimizing environmental pollution caused by sulfidic materials.

It has now been found that separation of the various metal sulfides in residual products from mining or metal manufacturing or in ores can be achieved in a surprisingly simple fashion by oxidation with hydrogen peroxide

the metal sulfides being converted to sulfates having different solubilities and/or oxides/hydroxides which may be recovered separately. Noble metals occluded in sulfide minerals, such as gold and/or silver, are liberated as a result of the conversion and thus, can be extracted as well.

The process is excellently suited for separating the residual products from copper slate smelting, and in a particularly preferred fashion, the process according to the invention can be used to separate the materials contained in Theisen sludge.

According to the invention, the aqueous hydrogen peroxide solution at a concentration of 5-45 vol.-%, preferably 25-35 vol.-%, is directly admixed to the moist Theisen sludge, and an exothermic reaction takes place. The temperature rises up to about 97°C where initially, the organic components will be oxidized. At the end of the reaction, a solid and a liquid phase are present. Nearly complete separation of zinc from lead is achieved, the lead sulfides being converted to sparingly soluble lead sulfate, the zinc remaining in solution in the form of hydrated sulfates. The radioactive substances follow the same path as

lead and are likewise concentrated in the solid phase, as are the oxidized organic components.

Figure 1 shows the distribution of the individual elements in % by weight between solid and liquid phase subsequent to oxidation of the Theisen sludge (left = solid phase; right = liquid phase) as a function of their overall content in the starting material.

A similar distribution of the metals contained in the ores is obtained in the treatment of sulfide ores where in addition, possibly occluded noble metals such as gold and/or silver are liberated.

In order to make the process more efficient, it is advantageous to subject the sulfidic starting materials to a mechanical pretreatment. According to the invention, they may be ground in order to reduce the grain size and provide new surfaces. The advantage of this is that the overall reaction will proceed more rapidly.

With Theisen sludges, it may also be advantageous to dry the starting material at a temperature of up to 70°C prior to the mechanical treatment.

It has been found that the process of the invention involving oxidation by hydrogen peroxide may be used both for sulfidic residual products from mining or metal manufacturing and for sulfide ores and the residues from the flotation thereof. The oxidation reaction using hydrogen peroxide is exothermic and may proceed under normal conditions (20°C and 1 bar). Obviously, process optimizing by modifying the pressure and/or the temperature is possible, depending on the starting material, and represents routine work for a person skilled in this field of the art. For turnover optimization, stabilizing substances such as sodium silicate may be added to the hydrogen peroxide solution.

According to the invention, one may even think of using another strong oxidizing agent instead of hydrogen peroxide, or even a mixture of hydrogen peroxide and a strong oxidizing agent.

The process according to the invention involves the advantage that environmentally hazardous residual products from mining or metal manufacturing may be processed in a simple fashion and at low cost. This applies to the Theisen sludge, in particular. The lead sulfate having formed may be used in further processes for metal production. The same applies for the zinc sulfate having formed. Moreover, it is possible to recover trace elements contained in the Theisen sludge, particularly rhenium.

In the case of Theisen sludge, the treatment with hydrogen peroxide also results in a considerable decrease of the concentrations of organic components. In particular, those of PAKs and biphenyls are changed in such a way that the corresponding B values of the "Dutch list" are no longer exceeded in the products.

In the case of sulfide ores and/or the flotation residues thereof, noble metals such as gold and/or silver are also liberated when using the process of the invention, and remain in the solid residue. Thus, a disintegration process for sulfidic ores and their processing residues is provided, which makes ultra-fine grinding for additional recovery of noble metals in the run-up to cyanide leaching unnecessary.

The invention is also directed to the innovative use of hydrogen peroxide in the separation of sulfidic materials and, in particular, for liberating noble metals from mono- or polysulfidic ores or flotation residues of polysulfidic ores.

Without intending to be limiting, the invention will be illustrated by way of embodiments.

**Example 1:**

37 g (30 g of dry substance) of a mixed sample of fresh, moist Theisen sludge (Deponie Helbra, Germany) was mixed with 300 ml of distilled water and processed mechanically (laboratory ball mill, steel balls, 350 rpm, 1 hour grinding period). Thereafter, the solids were removed by centrifugation (the residual water essentially contained alkalies, alkaline earths, sulfate) and dried at 65°C. 5 g of the material obtained above was mixed with 350 ml of hydrogen peroxide (30% vol.-%) and stirred continuously. The exothermic reaction reached its peak within 90 minutes (97°C). After fading of the reaction and sedimentation of the solids, the solids were filtrated (weight loss: 40%, residual liquid phase: 280 ml).

**Example 2:**

Herein, a polysulfide ore was treated, consisting of the ore minerals galena (Pb sulfide), sphalerite (Zn sulfide), chalcopyrite (Cu sulfide), as well as pyrite (Fe sulfide), and included amounts of sulfate and silicate minerals (barite, Ba sulfate). In addition, the ore contained 0.6 ppm of gold and 90 ppm of silver.

5 g of ore was ground in a laboratory ball mill and subsequently added with 100 ml of a 30% hydrogen peroxide solution. The vigorous reaction which began after about 5 minutes was highly exothermic; the temperature rose to 95°C. The reaction faded after less than 1 minute; further addition of 50 ml of solution resulted in a notably weaker reaction which likewise faded rapidly. This procedure was

repeated until no further reactions could be observed.

As a result, a pale bluish solution had formed, containing the metals copper, zinc and iron in the form of hydrated sulfates. In addition, a brown-gray residue had formed which contained the metals lead in the form of its sulfate and iron in the form of poorly crystallized oxide hydrates.

Zinc and copper at more than 75% (relative to the starting material) were determined to be the major components in the liquid phase. Lead was found in the solid phase at more than 99%. The minor components chromium and arsenic were found in the solid phase at more than 99%, and cadmium was found in solution at more than 75%. Gold and silver were found in the solid phase at more than 99%.

**Example 3:**

Herein, the residues from flotation processing of the ore from Example 2 ("tailings'), which at present are dumped as waste and give rise to the environmental pollution described above, were treated according to Example 2. The sample consisted of pyrite including minor residues of the other sulfides of the original ore. The reactions proceeded in a similar way as those described in Example 2. The solid residue essentially consisted of Fe oxide hydrates. Gold and silver had concentrated in the residue at more than 99%.

**THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:**

1. A process for separating different metals contained within sulfidic materials, said process being characterized in that an aqueous hydrogen peroxide solution is admixed with said sulfidic materials, resulting in an exothermic reaction in which organic components are oxidized, and when the reaction is complete, a solid and a liquid phase is formed, the reaction further being characterized in that no additional acid is added during the process.

2. The process according to claim 1, characterized in that residual products from mining or metal manufacturing are used as the sulfidic material.

3. The process according to claim 2, characterized in that Theisen sludges or residues from flotation of sulfide ores are used as the sulfidic material.

4. The process according to claim 1, characterized in that materials of natural origin are used as the sulfidic material.

5. The process according to claim 4, characterized in that poly- or monosulfidic ores are used as the sulfidic material.

6. The process according to any one of claims 1, 2, 4 and 5, characterized in that the sulfidic materials are subjected to a mechanical pretreatment.

7. The process according to claim 3, characterized in that the sulfidic materials are subjected to a mechanical pretreatment.

8. The process according to claim 6, characterized in that the mechanical pretreatment is grinding.

9. The process according to claim 7, characterized in that the mechanical pretreatment

is grinding.

10. The process according to any one of claims 1 through 6 and 8, characterized in that the hydrogen peroxide solution is used at a concentration of 5-45 vol.-%.

11. The process according to claim 7 or 9, characterized in that the hydrogen peroxide solution is used at a concentration of 5-45 vol.-%.

12. The process according to claim 10, characterized in that the hydrogen peroxide solution is used at a concentration of 25-35 vol.-%.

13. The process according to claim 11, characterized in that the hydrogen peroxide solution is used at a concentration of 25-35 vol.-%.

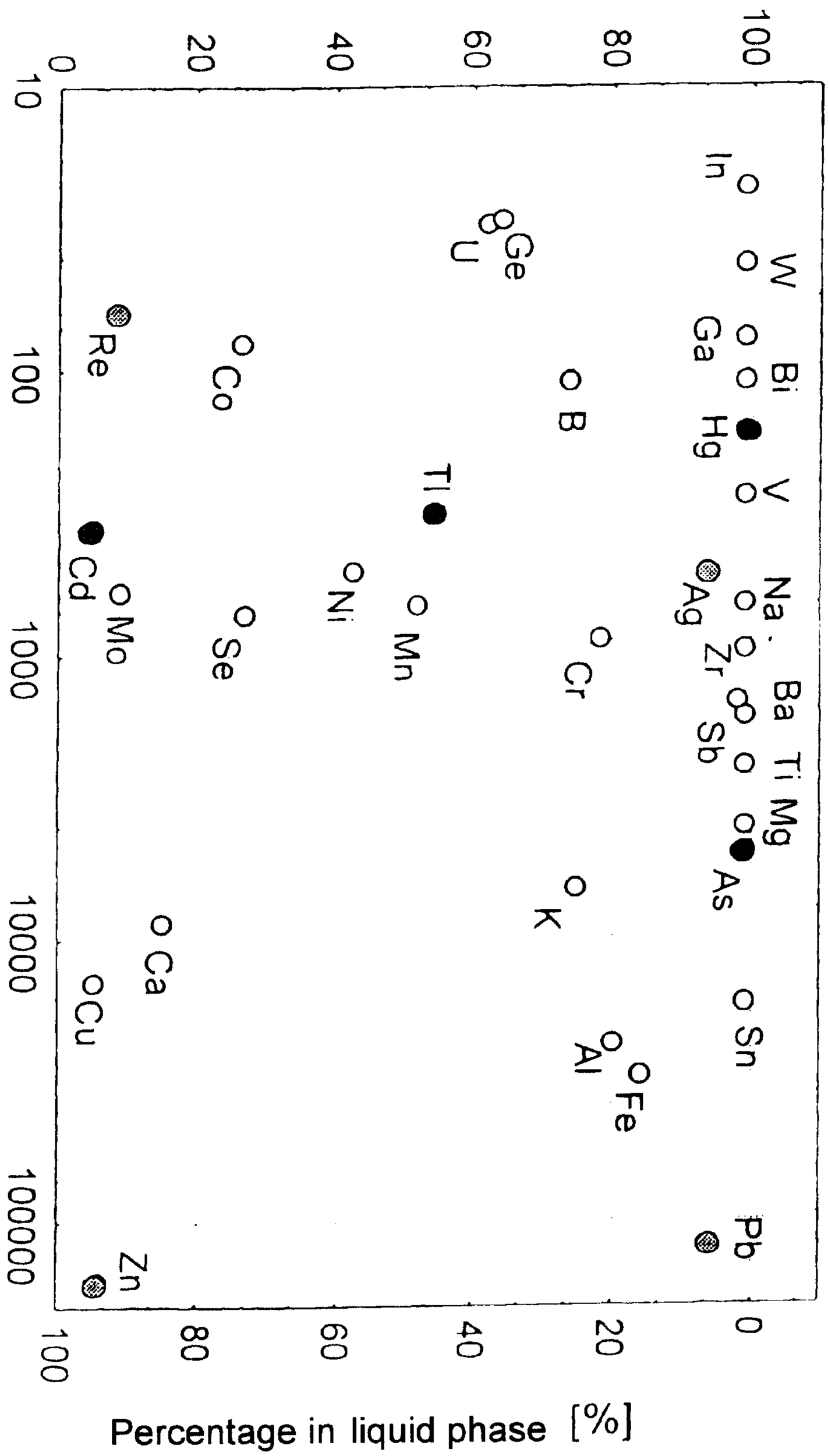
14. The process according to claim 10 or 12, characterized in that stabilizing substances are added to the hydrogen peroxide solution.

15. The process according to claim 11 or 13, characterized in that stabilizing substances are added to the hydrogen peroxide solution.

16. The process according to any one of claims 3, 7, 9, 11, 13 and 15 characterized in that the Theisen sludges are dried at a temperature of up to 70°C prior to said mechanical treatment.

17. Use of an aqueous hydrogen peroxide solution without acid additives for separating different metals contained within sulfidic materials.

18. The use according to claim 17, characterized in that residual products from mining or metal manufacturing, or materials of natural origin are used as sulfidic materials.


Element distribution pattern after reaction
Percentage in solid phase [%]
0
20
40
60
80
100
In
W
Bi
V
Ga
Hg
Ge
U
B
Tl
Re
Co
Na
Ba
Ti
Mg
Ag
Zr
Sb
As
Sn
Cr
K
Fe
Al
Mn
Ni
Se
Mo
Ca
Cd
Cu
Zn
Pb
10
100
1000
10000
100000
Original content [µg/g]
100
80
60
40
20
0
Percentage in liquid phase [%]