

International Journal of Mine Water, Vol. 5, No. 2, (1986), 43-56

Printed in Madrid, Spain

A STUDY OF THE DRAINAGES OF THE
PYRITE MINES OF ALJUSTREL (PORTUGAL)

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ABSTRACT

Characterization of the pollution charge of drainages from pyrite mines of Aljustrel (Portugal) was made. Laboratory experiments were performed in order to recover copper by cementation and remove iron, zinc and acidity by neutralization with lime. It was found that the removal of the metal ions is completed when pH reaches a step at 5.0-5.5, whichever the ratio between Fe(II) and Fe(III).

INTRODUCTION

Mine drainages often bring about severe problems. In the case concerning the pyrite mines of Aljustrel (Portugal) their drainages are a considerable pollution source and this is why a laboratory study was carried out in order to eliminate both their high acidity and iron content, and also to try to recuperate their appreciable amounts of copper and zinc, as much as possible. The study dealt with three drainages A, B and C, taken from the three main mines of Aljustrel's complex: Algaes (A), Feitais (B) and S.João + Moínho (C).

A literature survey concerning copper recovery points out three ways: solvent extraction, ionic exchange and selective precipitation. The first two techniques are too expensive considering that the copper concentration ranges in these waters are low, and the third is difficult to apply owing to the high iron concentration in the waters. Thus, we decided to try the copper recovery only by cementation (1, 5, 15 and 19).

With regards to the iron removal, the literature survey showed two potentially interesting processes: precipitation

either as goethite (6 and 7) or as jarosite (2, 12 and 13). However, because both processes must be carried out at high temperatures, we decided not to try them, as they were too expensive. Therefore, as an alternative, we decided to precipitate the iron, by the neutralization of the water until we obtained an adequate pH. It must be stressed that this method has the advantage of simultaneous removal of iron, zinc and acidity of the waters, and in this way the treated water can be discharged into a river without serious pollution problems.

Neutralization of mine drainages is usually done with the cheapest neutralizing agents, i.e., limestone or lime. Most of the consulted papers refer to the utilization of lime (3,9,10,11,20 and 21).

Economic recovery of zinc is rather questionable owing to the low concentration range of this element. Ionic exchange is inadequate on account of the high concentrations of other elements. Solvent extraction, in order to operate would require rather high zinc concentrations. Reverse osmosis was mentioned by Sastri and Ashbrook (16,17 and 18) as a possibility for the purification of acid mine drainages though its application seems doubtful. The recovery tried in this work is chemically feasible, though it does not seem economically attractive. The technique consisted in the solubilization of the zinc by leaching the precipitate obtained during the neutralization with a 20% NaOH solution.

EXPERIMENTAL

Alterations of the waters when exposed to the air

An aliquot of each sample was exposed to the air in a glass beaker. Determinations of pH, iron, copper and zinc were carried out. An Orion ionalyser, model 801, was used for pH measurements. Iron, copper and zinc concentrations were determined by atomic absorption spectrophotometry (An IL aa/ae spectrophotometer 551 was used).

Copper removal by cementation

Ten iron rectangular chips (10x25 mm) weighing about 31 grams were put in each of the 250 ml Erlenmeyer flasks containing 100 ml of the water to be tested. The flasks were placed on a shaker and the reaction was allowed to occur for selected periods of time. Copper, and sometimes zinc, were determined in the solution after filtration.

Similar tests were done though with a previous pH increase (≈ 1). This was achieved adding small portions of calcium carbonate, with constant stirring. As precipitates were observed, these were removed by filtration before carrying out the cementation.

Another group of tests was carried out but the pH increase was performed only after a two hours cementation. The precipitate was removed by filtration and the filtrate was analysed.

Iron removal by neutralization

Neutrations were carried out by addition of 15 or 1% (w:v) calcium oxide suspension. Iron, copper, zinc and pH determinations were performed in the filtered waters.

The influence of the Fe(II)/Fe(III) ratio upon neutralization was studied adding the oxidizing agent and letting it act during several periods of time before addition of the calcium oxide suspension.

Zinc removal

The precipitate obtained when neutralizing the water with calcium oxide suspension, was leached twice with a 20% NaOH solution.

RESULTS AND DISCUSSION

Alterations of the waters when exposed to the air

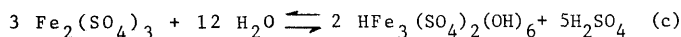
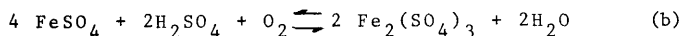
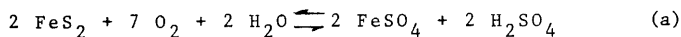
Table 1 gives some data concerning the initial composition of the samples.

Table 1. Initial composition of the samples

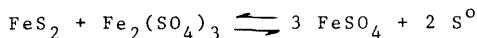
Sample	pH	Iron (ppm)	Copper (ppm)	Zinc (ppm)
A	2.0-2.5	5,200 - 5,700	300 - 320	1895 - 2900
B	2.0-3.5	130 - 375	8 - 12	160 - 250
C	2.0-3.0	65 - 590	0.7 - 0.8	150 - 360

A slight pH decrease and an increase in the iron, copper and zinc concentrations were noticed after exposure to the air. In order to understand this, some considerations will be made.

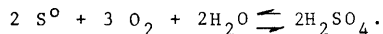
Drainages of sulphide ore mines, namely those of pyrites, have a composition similar to those shown in Table 1, the acidity being a consequence of the sulphur oxidation to sulphuric acid. From the rather extensive literature about these waters, it is interesting to draw attention to the papers of Thompson (20) and Boorman and Watson (4) who propose some mechanisms. The three main reactions involved in the production of sulphuric acid in the waters contacting pyrites, may be considered as follows:



The authors point out that reactions (a), (b) and (c) are chemical reactions, however, owing to the low reaction rate of reaction (b) at pH < 4.0, compared with its high rate in the presence of "Thiobacillus ferrooxidans", it can be admitted that reaction (b) is mainly bacteriological. It is important to realize that, while reactions (a) and (b) require aerobic conditions, reaction (c) can take place in anaerobic conditions. Maybe in the cases that we studied, reaction (b) has had small yield because Fe²⁺ predominated over Fe³⁺. Otherwise, the explanation for this fact may be found in the papers by Boorman and Watson (4) and Dutrizac and MacDonald (8). According to them, as the Fe³⁺ solutions (those resulting from reaction (b)) are an excellent leaching agent of ores (this may be quite important nowadays, for instance, in the case of uranium ores), the pyrites may react according to the following equation:



and, if so, Fe²⁺ will predominate again in the mine drainages. Concerning the elemental sulfur, S⁰, formed, it is oxidized to sulphuric acid in the presence of "Thiobacillus ferrooxidans" according to the following equation:



Another possible explanation for the presence of Fe²⁺ in the waters, could be the existence of much organic matter in the fields where they run through. It seems, however, that this is not the case of Aljustrel's mines.

The previous considerations allow us to find a possible explanation for the observations concerning the alterations of the waters through time. Initially, admitting that reaction (b) predominates in the aerobic conditions of the tests, we would expect to notice a pH increase owing to acid consumption in that reaction and an increase in Fe³⁺. Nevertheless, there was a slight pH decrease accompanied by an increase of turbidness and precipitation; both water and precipitate darkened as well. This draws attention to reaction (c), where sulphuric acid forms and ferric hydroxosulphates appear (these partly remain in colloidal state). The darkening of the colour suggests formation of ferric compounds.

An increase in the iron, copper and zinc concentrations was noticed (this was more pronounced in Algarès samples). A possible explanation is that the pH decrease may have dissolved those elements, eventually retained in the solid phase of the waters.

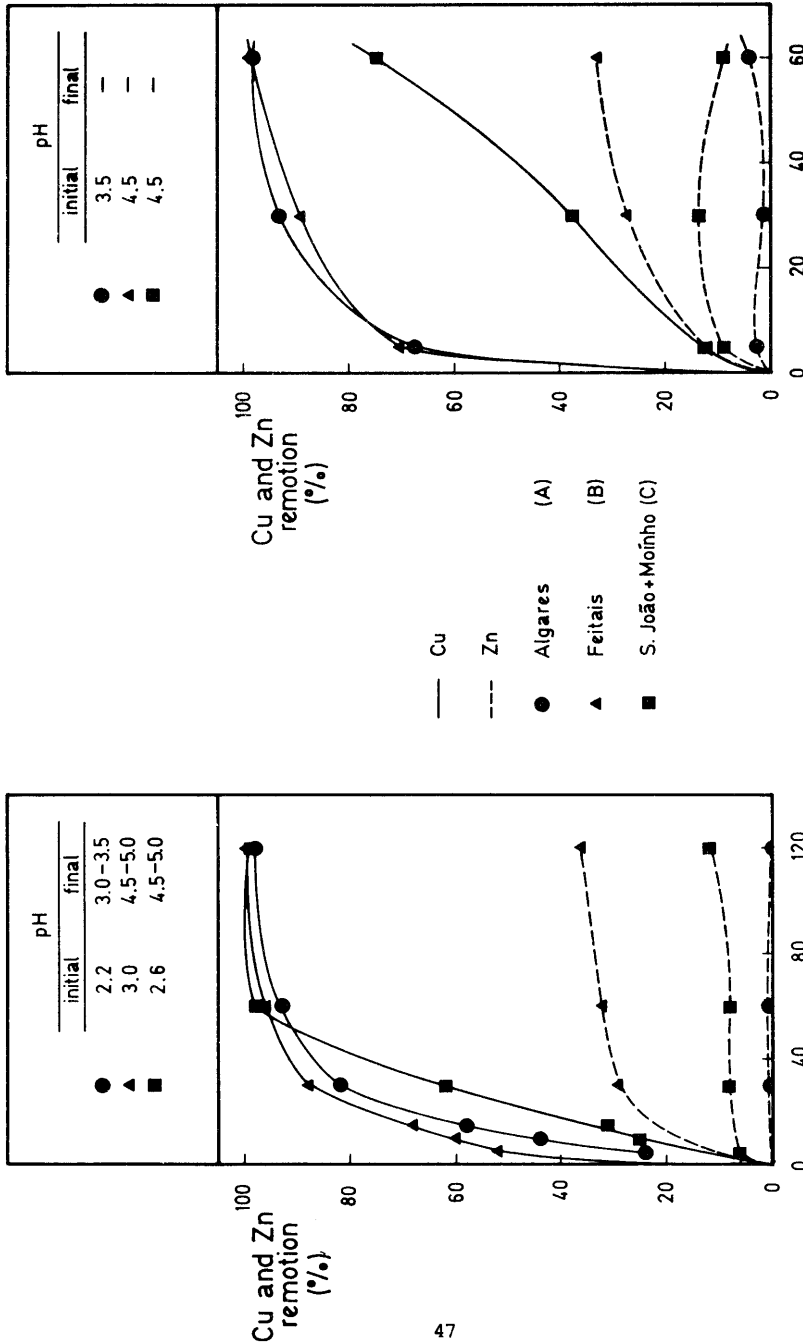


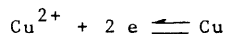
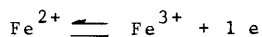
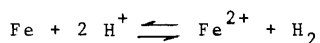
Figure 2. Removal of Cu and Zn vs. time of contact with iron in the cementation (initial pH higher than in Fig. 1.)

Figure 1. Removal of Cu and Zn vs. time of contact with iron in the cementation

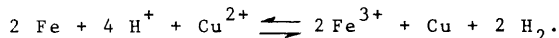
Copper removal by cementation

The results obtained are presented in Figures 1 and 2. It was shown that after a cementation period of 60 minutes, the copper recovery is already greater than 90%. Concerning Algaes' samples (the most important ones in this study) after one hour the recovery was 93%. Though there are other variables that influence this operation (area and physical state of exposed iron surface, water flow-rate, etc.), determination of the minimum time of contact is important as it will allow for economization of large amounts of iron. It was also noticed that zinc entrained by copper during cementation is negligible.

As it was expected, cementation caused a pH increase. Schematically, we can consider the following reactions:



or,



This decrease in acidity is desirable, but the iron concentration increase in the water is certainly not.

According to the experimental results it seems that there is no advantage in performing a neutralization previous to the cementation. Actually, as the neutralization causes precipitation and the precipitate has to be removed prior to the cementation process, such neutralization would therefore be troublesome. If cementation is carried out for two hours and then pH is raised (1.0 or 1.5 units) by means of CaCO_3 additions, copper removal is complete though iron and zinc still partly remain.

Iron removal by neutralization

The results obtained when neutralizing A, B and C waters with CaO are shown in Figures 3,4 and 5. Concerning Algaes' (A) water, it was observed that iron is practically all precipitated after addition of 21 grams of CaO /liter of water when pH 5.0-5.5 is reached. Traces of copper and zinc still remain (10 and 25 ppm, respectively). Further addition of 12 grams of CaO /liter of water precipitates copper quantitatively and only zinc traces remain (0.15 ppm). If pH is raised until about 13 (adding another 12 grams of CaO /liter of water) a slight zinc solubilization is observed, as it would be expected, owing to the zinc amphoteric character. Referring to B and C samples, there was a similar behaviour with a step at pH 5.0-5.5.

The amounts of CaO suspension spent to reach pH 5.0-5.5, fairly agree with those calculated under the assumption that

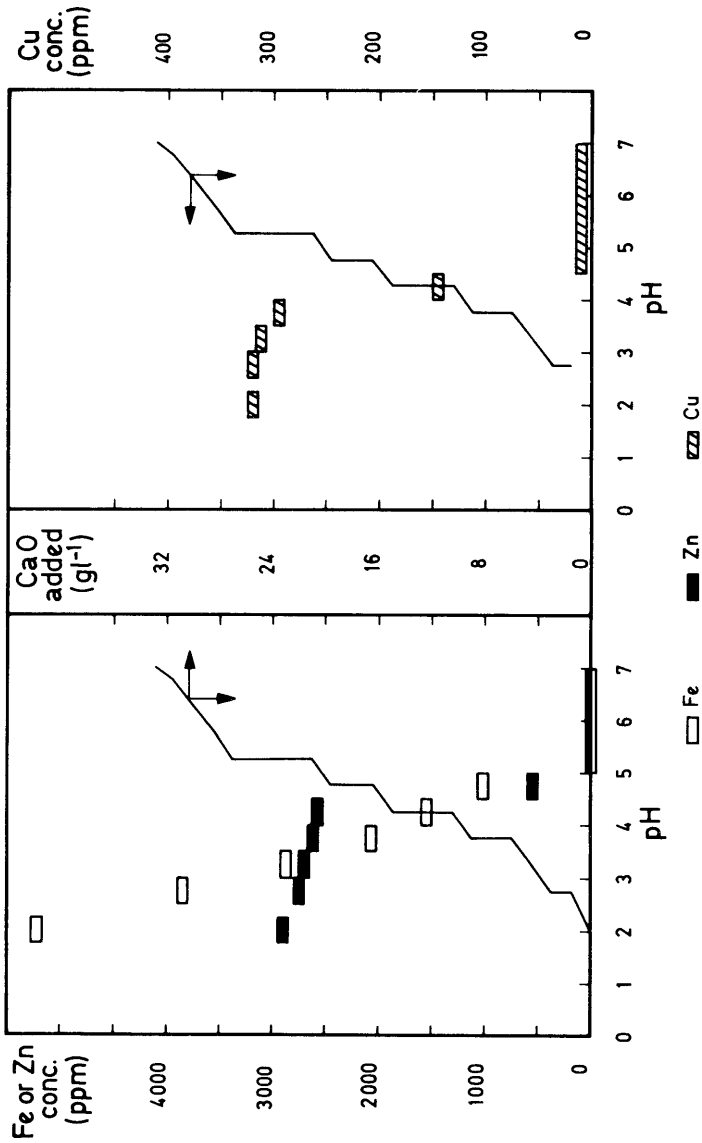


Figure 3. Neutralization curve and concentrations of Fe, Zn and Cu in solution vs. pH (Algalgae' water)

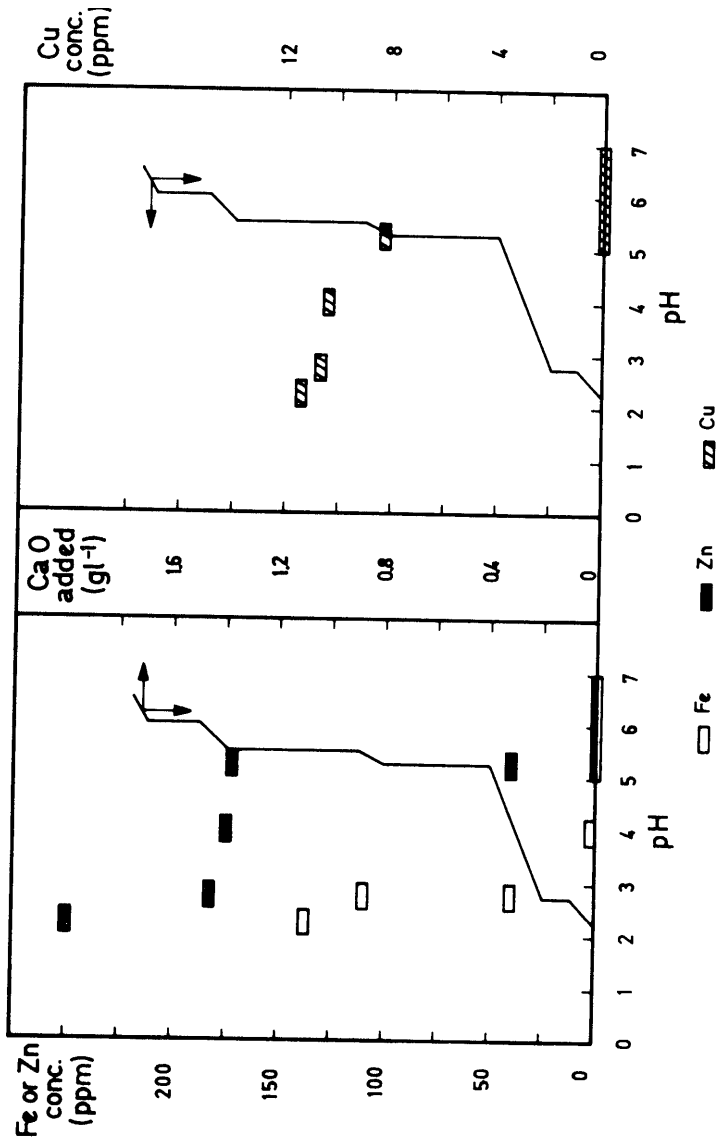


Figure 4. Neutralization curve and concentrations of Fe, Zn and Cu in solution vs. pH (Feitais' water)

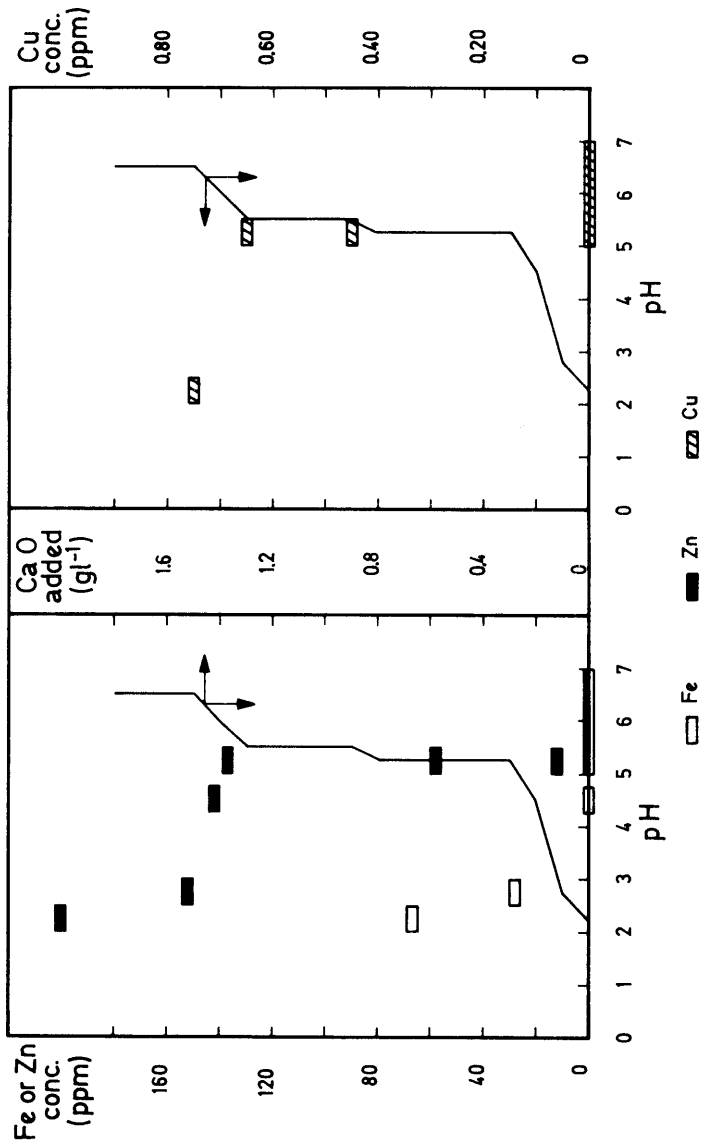


Figure 5. Neutralization curve and concentrations of Fe, Zn and Cu in solution vs. pH (S. João + Moínho's water)

the metal cations are precipitated as hydroxides. The existence of a large step at pH 5.0-5.5, i.e., the pH stabilization in a large range of CaO suspension additions, may be a consequence of Fe(II) and (III) hydroxosulphates formation. As a matter of fact, according to Nordstrom et al. (14) besides amorphous iron hydroxides, other solid phases may be formed in aqueous sulphate solutions: melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), copiapite ($\text{Fe}^{2+} \text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20 \text{H}_2\text{O}$), coquimbite² ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) and jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$). Although we have not experimental evidence, it may be admitted that the neutralization step observed at pH 5.0-5.5 in a medium that is rich in calcium and sulphate ions, may be due to the formation of solid hydroxosulphates presumably with hydroxyl metal ratios higher than those referred to above, as jarosite and copiapite precipitate at a lower pH.

An important conclusion to be drawn is that the precipitation of all the iron (Fe(II) and Fe(III)) is achieved when pH reaches 5.0-5.5. Indeed if Fe(II) were precipitated as $\text{Fe}(\text{OH})_2$ the precipitation should be completed only when $\text{pH} \approx 9$, that is to say that in actuality less CaO suspension is spent to remove the metal ions.

In order to study the influence of the Fe(II)/Fe(III) ratio in the water upon the iron precipitation, another set of tests was carried out in which partial oxidation was performed previous to the neutralization. As oxidizing agents, calcium hypochlorite, sodium peroxide, hydrogen peroxide and air were used. The widely spread settling times of the precipitates obtained in these experiments show that the Fe(II)/Fe(III) ratio is an important parameter which deserves attention in future research. As a general trend, it is observed that the settling time of the precipitate increases and compactness decreases with pH and Fe(II)/Fe(III) ratio.

Zinc removal

It was only tried to leach the precipitate obtained when neutralizing the water with the CaO suspension, with a 20% NaOH solution. After two extractions, 64% of total zinc was recovered and certainly a higher yield would be achieved if more extractions had been made.

Analyses of neutralized waters

The three samples, A (previously cemented), B and C, were neutralized with CaO suspension up to $\text{pH} \approx 7.0$, the precipitates allowed to settle and, after filtration, the filtrates were analysed. The results obtained are shown in Table 2.

Table 2. Analyses of A*, B and C waters after neutralization with CaO suspension up to pH \approx 7.0

Determination	Water		
	A*	B	C
pH	6.5	6.5	7.0
Dry residue (ppm)	4,134	5,054	4,656
Calcined residue (ppm)	3,642	4,489	4,294
Silica (SiO ₂) (ppm)	1.6	2.8	0.8
Alumina (Al ₂ O ₃) (ppm)	4.7	3.9	4.3
Calcium (Ca) (ppm)	725	672	1,034
Magnesium (Mg) (ppm)	239	87	48
Chlorides (Cl ⁻) (ppm)	37	64	50
Sulphates (SO ₄ ²⁻) (ppm)	2,694	1,948	3,043
Acidity to phenolphthalein (ppm)	0.16	0.14	0.18
COD (ppm)	5.1	1.8	0.1
Lead (Pb) (ppm)	0.1	0.1	0.1

* Previously cemented.

CONCLUSIONS

Drainages from three pyrite mines of Aljustrel (Portugal) are very acid, they have rather high iron and zinc contents and, sometimes, not negligible copper concentrations.

Laboratory experiments using lime (1 and 15% CaO suspensions) in order to neutralize acidity and precipitate iron and zinc, were made.

When copper content was high, more than 90% of this element was recovered by cementation in acid medium with iron scrap.

It was found that neutralization proceeds by steps and when the step at pH 5.0-5.5 is reached, the water is practically iron and zinc free.

The zinc recovery from the precipitate obtained, was tried by leaching it with NaOH solution. Although more than 60% of zinc was recovered with a two-stages leaching, this process is not economically viable.

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