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STUDY OF ZINC AND COPPER REMOVAL BY IRON (III) AND (II) OXYHYDROXIDES

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ABSTRACT

Zinc and copper removal by iron (III) and (II) oxyhydroxides as a function of pH (5.0-12.5 range) and iron suspension concentration, was studied. The influence of calcium presence, as calcium chloride, nitrate or sulphate, was investigated. A similar study dealing with copper removal was carried out, though only at pH 6.0 and with a "standard" suspension concentration.

INTRODUCTION

The adsorption of heavy cations by iron, aluminium, titanium, silicium and manganese oxyhydroxides has been studied by several research workers namely, Murray, Healy and Fuerstenau (1968), Van der Giessen (1968), Gadde and Laitinen (1973 and 1974), Lee (1975), Bar-Yosef, Posner and Quirk (1975), Bilinski (1976), Kinniburgh, Jackson and Syers (1976), Forbes, Posner and Quirk (1976), Shuman (1977), Davis and Leckie (1978), Kinniburgh and Jackson (1980), Gray (1981), Laxen and Sholkovitz (1981), Millward and Moore (1982) and Lortie, Klvana and Paris (1983). In our research centre this study appeared as a consequence of another one previously undertaken to diminish the acidity and the high iron and zinc contents of the drainage water of the pyrite mine of Aljustrel (Portugal). As, when the neutralization of the above mentioned water is carried out, iron (III) oxyhydroxide forms, and because this has adsorbent properties, we decided to investigate the extension of zinc removal by the precipitated iron (III) oxyhydroxide. Therefore, a plan was elaborated in order to establish the relationship between pH and the degree of zinc removal. As in the preliminary studies the neutralization has been done with a calcium oxide suspension, several tests were visualized in order to show the calcium influence either as calcium chloride, nitrate or sulphate. A wide pH range (5.0-12.5) was studied. The influence of the iron suspension concentration upon its zinc adsorption capacity was studied, too.

Since the drainage water of the above mentioned mine contains iron (II) besides iron (III), tests with iron (II) oxyhydroxide were also carried out in order to clarify which one is the best discontaminating agent: iron (II) oxyhydroxide or iron (III) oxyhydroxide.

As in the cited drainage water there is a valuable polluting element, copper, similar adsorption studies were performed for this cation, though only at pH 6.0 and with the "standard" suspension concentration.

EXPERIMENTAL

Preparation of iron (III) and (II) oxyhydroxides

From now on, iron (III) oxyhydroxide will be abbreviated as I(III) OH, and iron (II) oxyhydroxide as I(II) OH.

In order to prepare iron (III) oxyhydroxide, a process similar to that mentioned by Gadde and Laitinen (1973) was followed. By means of a pipette a 50.00 ml sample of 0.100 M $Fe(NO_3)_3$ solution was transferred into a 100 ml beaker. Then, from a burette, NaOH ≃ 0.1 M was added, drop by drop, constantly mixing with a magnetic stirrer, until the wanted pH value was reached. The pH control was done by means of an Orion Research Model 701A pH meter. The precipitate was allowed to settle during 3 hours and filtration through No.1 Whatman filter paper followed. The precipitate was washed with distilled water with the same pH of the suspension. After washing, the precipitate was transferred into a 1000 ml beaker with a jact of the pH adjusted water. The final volume was 640 ml. This suspension will be designated as having "standard" concentration.

Iron (III) oxyhydroxide suspensions with concentrations that are two and three times the "standard" one, were prepared similarly though using two and three times 50.00 ml samples of $Fe(NO_3)_3$ 0.100 M.

Iron (II) oxyhydroxide preparation was done in a way very similar to the previously referred to, though it has been necessary to use an inert atmosphere (nitrogen) as iron (II) easily oxidizes to iron (III). A 0.100 M $FeSO_4.7H_2O$ solution was used to start with.

Preparation of standard zinc solutions

Six standard zinc solutions with concentrations, respectively, 32.7, 65.4, 98.1, 130.8, 163.5 and 196.1 ppm were prepared. $ZnSO_4.7H_2O$ p.a., Merck, was used.

Tests

1. With zinc

50.00 ml samples of the I(III)OH "standard" suspension were thrown into 100 ml beakers. With a pipette, 20.00 ml of each of the standard zinc solutions were added. The mixture was stirred and equilibrium allowed to settle (4 hours). Filtration followed and zinc was analysed in the filtrate by atomic absorption spectrophotometry.

Later on, similar tests were undertaken though in the presence of calcium, either as calcium chloride, nitrate or sulphate.

The initial calcium concentration was always the same (0.015 M, what corresponds, approximately, to saturation with calcium sulphate).

After this other tests were carried out though with higher suspension concentrations: two and three times the "standard" one.

Tests using I(II)OH, maintaining an inert atmosphere (nitrogen), were performed, too.

2. With copper

50.00 ml samples of the "standard" I(III)OH suspension were thrown into 100 ml beakers. Suitable amounts of solid $CuSO_4.5H_2O$ were added in order to get the following Cu concentrations: 54.5, 108.9, 217.8 and 326.8 ppm (these values are similar to those that exist in the drainage water of the pyrite mine of Aljustrel). Stirring was provided and equilibrium allowed to establish (4 hours). Filtration was carried out and copper was analysed in the filtrate by atomic absorption spectrophotometry.

Similar tests were carried out, using copper in the presence of calcium derived from calcium chloride, nitrate or sulphate. As in the previous case of zinc, the initial calcium concentration was always the same (0.015 M).

Later on, tests were undertaken using I(II)OH suspension instead of I(III)OH, maintaining an inert atmosphere (nitrogen), as it has been already mentioned.

RESULTS

The experimental results obtained until pH 7.5, are summarized in the presented graphs. For higher pH values zinc precipitation occurs and consequently, adsorption will not be the only means of zinc removal. The results for this higher pH range (9.0-12.5) are shown in Table 1.

If C_{in} represents the initial zinc concentration and C_e the equilibrium zinc concentration in the solution, the graphs point out the linear relationship between $\log(C_{in}-C_e)$ and $\log C_e$.

Figures 1 and 2 show both the effect of pH and calcium presence (originated from calcium chloride, nitrate or sulphate), in zinc adsorption by "standard" I(III)OH suspension.

Figure 3 shows the effect of I(III)OH suspension concentration, at pH 6.0, in zinc adsorption.

Figure 4 shows the comparison between zinc adsorption by I(III)OH suspension and I(II)OH suspension with "standard" concentration for several pH values (5.0, 6.0 and 7.5).

In order to know the influence of the calcium concentration upon the zinc adsorption by the I(III)OH suspension with "standard" concentration, at pH 6.0, its initial concentration (when derived from calcium chloride) was doubled (0.015M → 0.030M). It was observed that the adsorption percentage that was around 40%, decreased noticeably moving to 0-10% range. A still higher calcium concentration has been tried (0.045 M), however, the results were similar to those obtained before (0.030 M).

Tests carried out with aged I(III)OH suspension (8 days) with "standard" concentration, pH 5.0 and 6.0, revealed a rather small increase in the zinc adsorption.

Table 1. Zinc removal by "standard" I(III)OH suspensions in the 9.0–12.5 pH range

pH	Initial concn. Zn^{2+} (ppm)	Zn^{2+} only	Zn^{2+} + Ca^{2+}		
		$\%Zn^{2+}$ removed	$\%Zn^{2+}$ removed		
			Cl^-	NO_3^-	SO_4^{2-}
9.0	9.3	99.7	99.5	99.2	99.5
	18.7	99.7	99.5	98.9	99.4
	28.0	99.7	99.5	99.7	99.7
	37.4	99.8	99.7	99.5	99.0
	46.7	99.9	99.6	99.6	98.5
	56.0	99.8	98.5	99.4	96.8
11.0	9.3	99.7	99.7	100.0	99.8
	18.7	99.9	99.9	100.0	99.4
	28.0	99.7	99.9	99.9	99.8
	37.4	99.5	99.9	99.9	99.9
	46.7	99.9	99.9	99.9	100.0
	56.0	100.0	99.9	100.0	99.9
12.5	9.3	99.5	99.8	99.7	100.0
	18.7	99.5	99.4	99.4	100.0
	28.0	95.3	94.7	99.6	100.0
	37.4	94.1	92.0	99.0	100.0
	46.7	93.8	87.3	93.6	100.0
	56.0	88.4	87.5	93.8	100.0

Figures 5 and 6 refer to copper adsorption, in the absence or presence of calcium (as calcium chloride, nitrate or sulphate) by I(III)OH and I(II)OH suspension, at pH 6.0, with "standard" concentration, respectively.

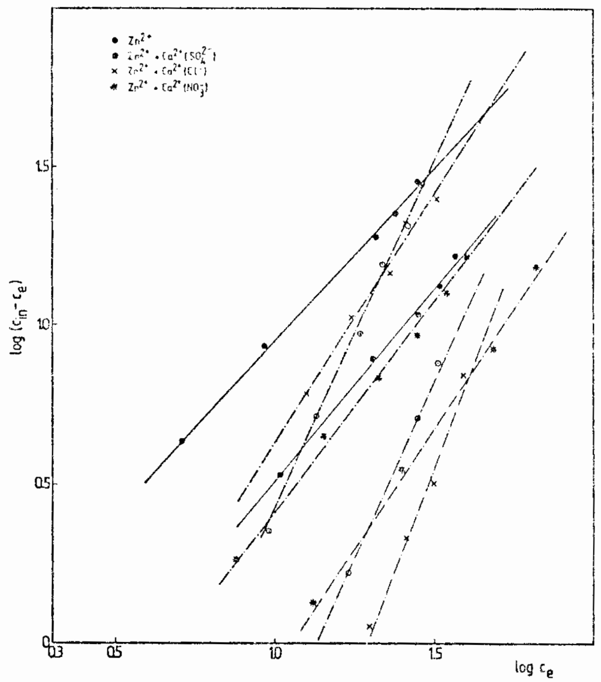


Fig.1. Zinc adsorption by I(III)OH with "standard" concentration, in the absence or presence of calcium, at pH 5.0 (—, — - —) and pH 5.5 (—, — · —)

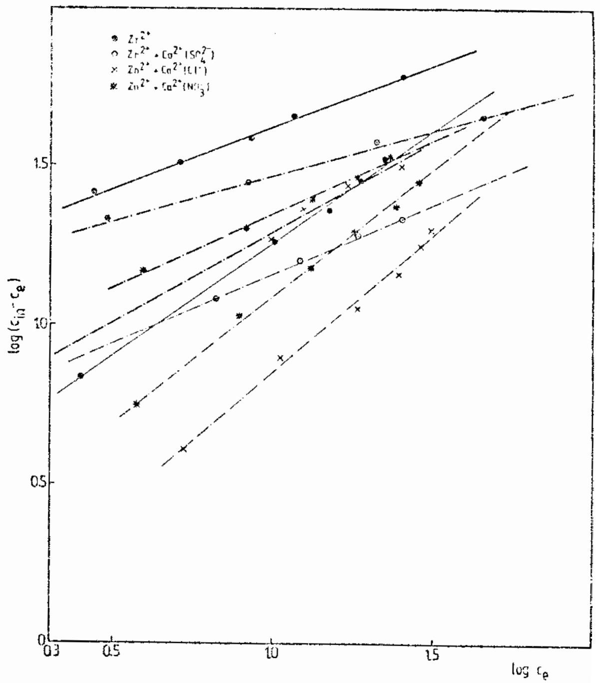


Fig.2. Zinc adsorption by I(III)OH with "standard" concentration, in the absence or presence of calcium, at pH 6.0 (—, - - - -) and pH 7.5 (—, — · —)

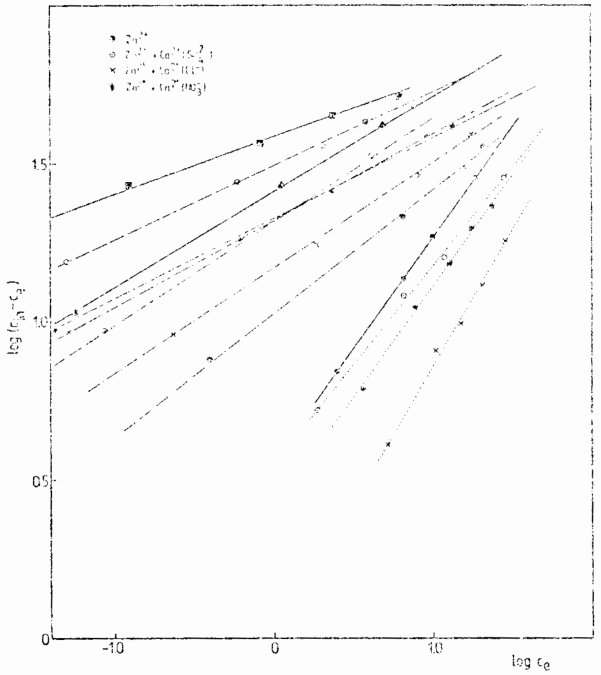


Fig. 3. Zinc adsorption in the absence (-◆-, -▲-, -□-) or presence of calcium (·····, —·····, —·-·-·-), by I(III)OH, at pH 6.0, with "standard", twice and three times the "standard" concentration, respectively.

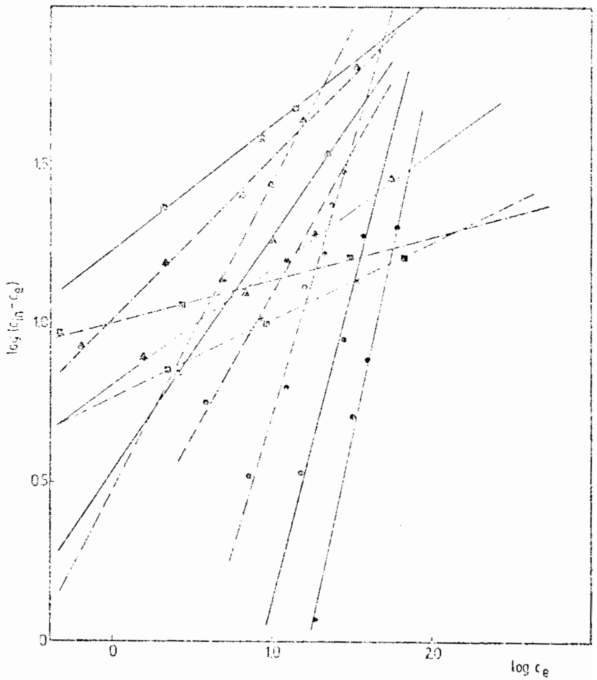


Fig. 4. Zinc adsorption in the absence (—, —·—) or presence of calcium (—, -- —), by I(III)OH and I(II)OH, respectively, at pH 5.0 (●), 6.0 (▲) and 7.5 (■).

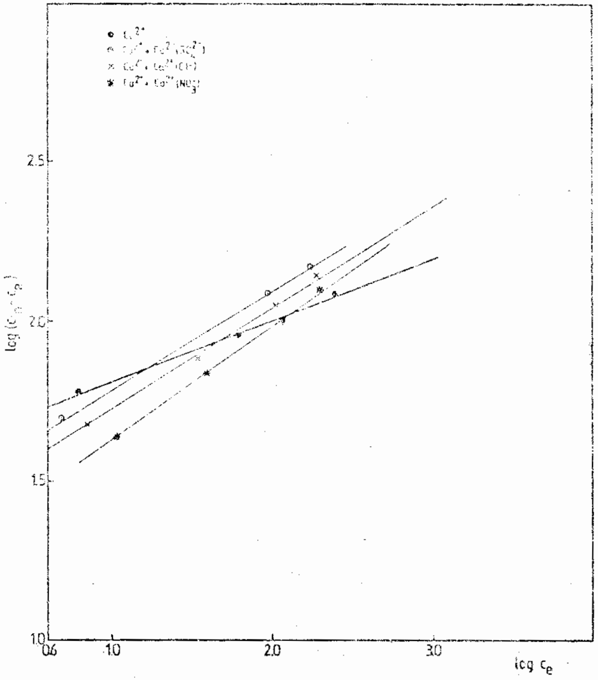


Fig. 5. Copper adsorption by I(III)OH with 'standard" concentration, at pH 6.0, in the absence or presence of calcium.

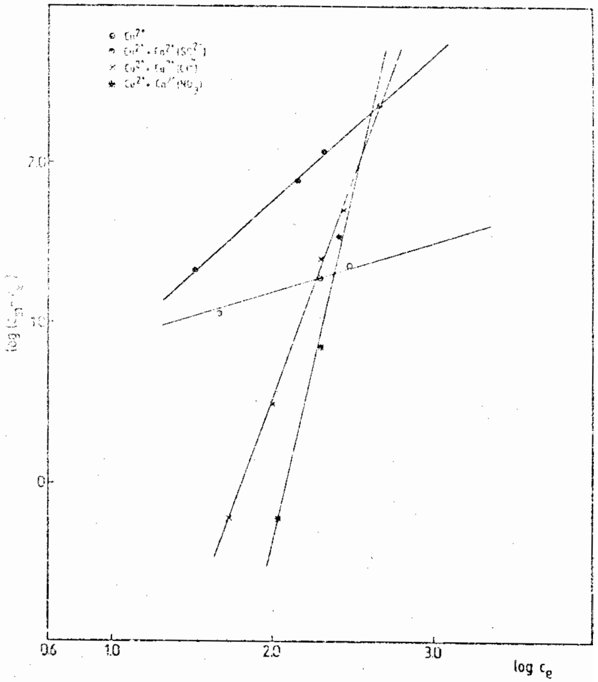
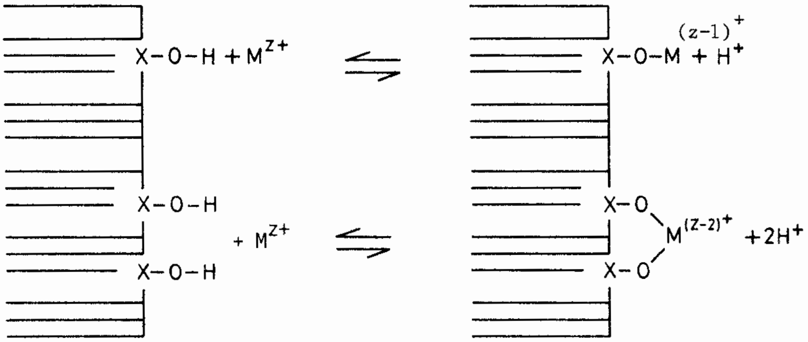


Fig. 6. Copper adsorption by I(III)OH with "standard" concentration, at pH 6.0, in the absence or presence of calcium.

DISCUSSION OF THE RESULTS

Despite the fact that, as already mentioned, the sorption of metal ions by several oxyhydroxides namely iron, manganese, titanium, silicium and aluminium, natural or synthetic ones, has been studied by several authors, the truth is that, until now, it has not been possible to explain all the obtained results with a simple theory. The validity of the proposed models is, then, restricted. In our case, for the pH and concentration ranges studied, the Freundlich equation is quite suitable.

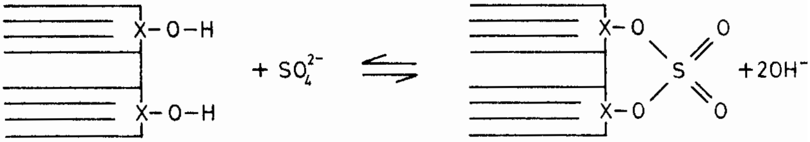
In order to interpret the zinc and copper adsorption by iron oxyhydroxide, one can accept a mechanism involving surface ionization (deprotonation of the surface hydroxyl groups) and complexation of the dissolved metal ions. Several species may form simultaneously. In a schematic way, one can accept the following mechanism:



where

X —— Fe
M —— dissolved metal (in our case Zn and Cu(II)).

Concerning anion interaction with iron oxyhydroxide, it is admitted that all bivalent oxyanions (we only studied sulphate), with the exception of tellurate, directly coordinate two surface iron cations, and the symmetry of the free oxyanion plays an important role in the determination of the configuration of the resulting complex, Sigg and Stumm (1980,1981) and Harrison and Berkheiser (1982). Each bidentate complex forms by substitution of hydroxyl groups. That is:



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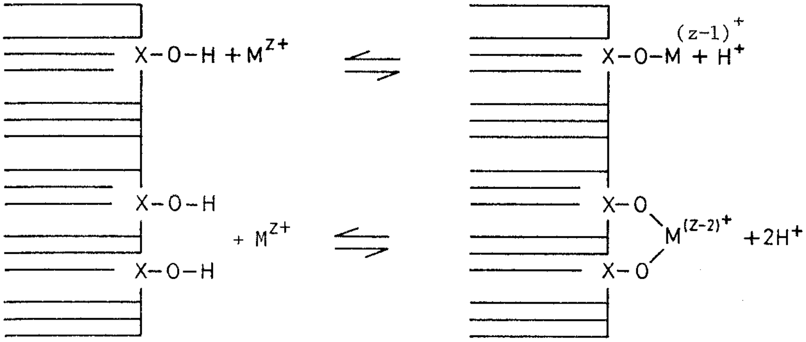

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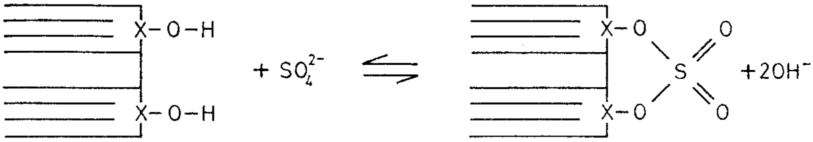

It is admitted that the monovalent oxyanions (we only studied nitrate) are mainly adsorbed by electrostatic interactions with the surface , though other secondary interactions have to be considered.

In order to visualize more easily pH influence upon the percentage of zinc removal by iron (III) oxyhydroxide (suspension with "standard" concentration) for the concentration range studied, attention is drawn to the following results (Table 2).

Table 2. pH influence upon the percentage of zinc removal by "standard" I(III)OH suspension

pH	Zn^{2+} only %Zn^{2+} removed		Zn^{2+} + Ca^{2+} %Zn^{2+} removed					
			Cl^-		NO_3^-		SO_4^{2-}	
	*	**	*	**	*	**	*	**
5.0	10.0	33.4	8.0	12.2	6.0	15.0	2.6	18.0
5.5	45.2	50.0	9.0	40.6	19.8	28.6	34.8	48.2
6.0	73.2	60.8	43.2	45.2	60.4	49.2	84.0	50.0
7.5	96.0	79.6	78.6	55.4	90.4	58.8	88.0	55.0
9.0	99.7	99.8	99.5	98.5	99.2	99.4	99.5	96.8
11.0	99.7	100.0	99.7	99.9	100.0	100.0	99.8	99.9
12.5	99.5	88.4	99.8	87.5	99.7	93.8	100.0	100.0

* These values are for an initial zinc concentration equal to 9.3 ppm.

** These values are for an initial zinc concentration equal to 56.0 ppm.

As it is shown above, until pH 7.5, there is a very marked pH influence upon the percentage of adsorbed zinc for the studied concentration range - when pH increases, the percentage of removed zinc increases, too. However, while at pH 5.0 and 5.5 the percentage of adsorbed zinc is a function that increases with the initial concentration, at pH 6.0 and 7.5 this function is a decreasing one (except at pH 6.0 when calcium from calcium chloride is present, in the zinc initial concentration range 37.4-56.0 ppm). In any situation, pH 5.0, 5.5, 6.0 and 7.5, the calcium presence (as calcium chloride, nitrate or sulphate) diminishes the quantity of removed zinc.

At pH 9.0, zinc removal is nearly complete, mainly if calcium is absent. At pH 11.0, zinc removal is, in any circumstances, practically 100%. However, at pH 12.5 a decrease in the efficiency of zinc removal was noticed, except when calcium sulphate is present.

The influence of the I(III)OH suspension concentration (pH 6.0) upon the zinc removal efficiency is pointed out next (Table 3).

Table 3. Influence of the I(III)OH suspension concentration (pH 6.0) upon the zinc removal efficiency

Suspension concentration	Zn^{2+} only %Zn^{2+} adsorbed		Zn^{2+} + Ca^{2+} %Zn^{2+} adsorbed Cl^-		NO_3^-		SO_4^{2-}	
	*	**	*	**	*	**	*	**
"Standard"	73.2	60.7	43.3	45.2	60.4	49.1	83.9	50.2
Twice "standard"	99.5	86.2	97.5	68.8	99.0	63.0	99.1	82.0
Three times "standard"	99.8	88.8	100.0	76.3	99.5	71.8	100.0	85.1

* and ** have the same meaning as in Table 2.

When only zinc is present, the percentage adsorption of this cation decreases with initial zinc concentration in any case: "standard" concentration of the suspension, two or three times the "standard" one. Generally speaking, calcium presence (no matter the nature of the anion associated with it) decreases the percentage adsorption of zinc. When the concentration of the suspension rises up to a value that is twice the "standard" one, the percentage adsorption of zinc increases substantially. However, when the suspension concentration rises up to three times the "standard" one, the additional increase in zinc adsorption has negligible meaning.

Comparison between the adsorbent effects of "standard" I(III)OH and I(II)OH suspensions at pH 5.0, 6.0 and 7.5 will be made easier observing the table that follows (Table 4).

Table 4. Comparison between the adsorbent effects of "standard" I(III)OH and I(II)OH suspensions at pH 5.0, 6.0 and 7.5

	I(III)OH				I(II)OH			
	Zn^{2+} only		Zn^{2+}+Ca^{2+} (SO_4^{2-})		Zn^{2+} only		Zn^{2+}+Ca^{2+} (SO_4^{2-})	
pH	%Zn^{2+} adsorbed				%Zn^{2+} adsorbed			
	*	**	*	**	*	**	*	**
5.0	10.0	33.4	2.6	22.0	60.6	59.0	35.8	50.0
6.0	73.2	60.7	83.9	50.2	93.2	73.7	83.0	73.2
7.5	96.1	79.7	88.0	55.0	96.4	18.8	76.5	9.0

* and ** have the same meaning as in Tables 2 and 3.

It can be concluded that while I(II)OH acts as a rather better zinc adsorbent than I(III)OH in the acid zone (pH 5.0 and 6.0), it is worse in the alkaline zone (pH 7.5).

The results for copper adsorption may be summarized as follows in Table 5.

Table 5. Copper adsorption by "standard" I(III)OH and I(II)OH suspensions at pH 6.0, in the absence or presence of calcium

	Cu^{2+} only $\%Cu^{2+}$ adsorbed		$Cu^{2+}+Ca^{2+}$ $\%$ Cu^{2+} adsorbed					
			Cl^-		NO_3^-		SO_4^{2-}	
	*	**	*	**	*	**	*	**
I(III)OH, pH 6.0, "std" concn.	96.3	37.9	87.1	43.4	80.0	40.8	91.1	47.4
I(II) OH, pH 6.0, "std" concn.	49.1	35.7	7.0	6.3	14.3	15.3	22.1	6.6

* These values are for an initial copper concentration equal to 54.5 ppm.

** These values are for an initial copper concentration equal to 326.8 ppm.

When using I(III)OH suspensions at pH 6.0 and with "standard" concentration, the following conclusions can be drawn:

1. For an equal molar concentration (6/7 mM) and in calcium absence, copper is rather more adsorbed than zinc (96.3% comparetively with 60.7%).
2. Calcium presence diminishes the percentage of copper adsorption, similarly to what happens with zinc. For the above mentioned concentration, the value 96.3 decreased down to 87.1, 80.0 and 91.1, respectively, when calcium is present as calcium chloride, nitrate or sulphate. Remember that, for zinc, the initial value of 60.8% decreased down to 45.2, 49.2 and 50.0, respectively.
3. Variation of copper concentration (in calcium absence) has a more pronounced effect upon adsorption than when zinc is concerned, in the concentration ranges studied. That is to say, while a zinc concentration increase to sixfold the initial value (9.3 → 56.0 ppm) causes a decrease down to 1.2 times less in the percentage of adsorption (73.2 → 60.8%), a similar relative variation of initial copper concentration (54.5 → 326.8 ppm) causes a decrease in copper adsorption down to 2.5 times less (96.3 → 37.9%).

Concerning the utilization of I(II)OH suspensions, at pH 6.0, with "standard" concentration, it can be concluded that:

1. For an equal molar concentration (6/7 mM), and in calcium absence, zinc is more adsorbed than copper (73.7% comparetively with 49.1%), contrarily to what happens with I(III)OH suspensions, at pH 6.0, with "standard" concentration.

2. Calcium presence decreases the percentage of copper adsorption. For the above mentioned concentration, the value 49.1% diminishes to 7.0, 14.3 and 22.1%, respectively, when calcium is present as calcium chloride, nitrate or sulphate. In the last situation, that is, when calcium sulphate is present (the most importante case for us, owing to the nature of the drainage mine water already mentioned), the percentage of zinc adsorption only changed from 73.7 to 73.2%, though for copper the influence was much more apparent: 49.1 to 22.1%.

3. Variation of copper concentration (in calcium absence) has a slightly more marked effect in adsorption than variation of zinc concentration, in the concentration ranges studied.

Remember that, a simple, expeditious way to draw conclusions dealing with the capacity and intensity of adsorption, is to observe the linear graphs corresponding to the Freundlich equation, $\log(c_{in}-c_e)$ versus $\log c_e$, because the ordinate at the origin gives an approximate indication of the adsorption capacity, and the slope indicates the adsorption intensity.

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