

Adsorption and desorption of lanthanum at sulfide mineral surface

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(Received November 10, 1988)

Abstract—Batch adsorption experiment with four sulfide minerals — Chalcocite galena, pyrite and sphalerite — were used to study for the adsorption and desorption behavior of La (III) in the presence of EDTA, a model humic matter. Linear adsorption was found in all cases.

The presence of soluble organic complexing ligand should reduce the mobility of La (III) in porous media and its transport to groundwater in the percolating soil solution. Binding mechanism is proposed to account for this preferential binding behavior.

Keywords: lanthanum; adsorption; sulfide mineral surface.

INTRODUCTION

The lanthanides, a set of important elements, are extensively dispersed among rocks and minerals. Lanthanides are surface mined, similar to other ores. Sulfide minerals may be present in the same ore deposit. Lanthanides are widely used in commerce, agriculture, and industries. Leachate from lanthanide tailing piles may pose a threat to both surface and groundwater quality. The degree of bioaccumulation and the toxicity of lanthanides to biota, however, is poorly understood.

The sulfide minerals are important constituents of soil, sediments, and aquifer materials and their interaction with the lanthanides is unknown. The transport and transformation of lanthanides in the environment is an important research area.

In this paper, we report our studies of the adsorption and desorption behavior of La (III) on four sulfide minerals as influenced by pH and the presence or absence of a soluble organic complexing agent, the disodium salt of ethylenediaminetetraacetic acid (EDTA).

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MATERIALS AND METHODS

Sulfide mineral preparation: pyrite, sphalerite, galena, and chalcocite were obtained from the Ward's Scientific Establishment. All minerals were examined by X-ray powder diffraction and only minor impurities were found (less than 5%). The minerals were crushed and sieved into four fractions using a nested set of Tyler standard stainless-steel mesh sieves. The surface area was determined by the ethylene glycol monoethyl ether method (EGME method) as described by Heilman *et al.* (1966). Physical data for the four sulfide minerals are given in Table 1.

Table 1 Physio-chemical properties of four sulfide minerals (Lin *et al.*, 1988)

Properties	Mineral type			
	Pyrite	Galena	Chalcocite	Sphalerite
Formula	FeS ₂	PbS	Cu ₂ S	ZnS
Part. Size* (μ)	<53	<53	<53	<53
Surface area (m ² /g)	4.8	2.0	3.1	2.5
Exchange sites (μ mole/g)	95.5	74.5	55.1	79.9
pH _{zpc}	4.41	7.44	7.47	7.10
pH _n **	2.46	5.98	6.06	5.62
pK _{a1}	3.50	5.26	5.25	5.08
pK _{a2}	5.32	9.62	9.68	9.13
pK _{a3}	9.81			
Solubility product	1.0×10^{-17}	3.4×10^{-28}	2×10^{-47}	1.2×10^{-23}
Mineral *** solubility	4.9×10^{-4}	8.6×10^{-5}	1.19×10^{-4}	6.5×10^{-5}

* The size of particles is the size of sieve in the experiment.

** pH of the natural mineral in water; a solid to water ratio of 1.1 was used to measure pH.

*** The mineral solubility is the solubility in water at 25°C, (g/100ml), (g mol/kg).

Adsorption isotherm methodology

Stock solution of La(NO₃)₃ with a concentration range of 10⁻³ to 10⁻⁵ moles/liter were prepared using Fisher Certified Grade chemicals and nanograde deionized water. Calcium nitrate was used to provide a background electrolyte and to simulate the median concentration of calcium in groundwater (Brown, 1986). The required working solution was prepared by dilution of the stock solution. Six different initial concentration (2 × 10⁻⁵ mol/L to 2 × 10⁻⁴ mol/L) of La (NO₃)₃ usually were prepared. The nitrate salt was used to limit or prevent the formation of ion pair in solution.

A mixture of 0.5 ml of 10⁻⁴ mol/L La (NO₃)₃ and 24.5 ml of 0.001 mol/L Ca (NO₃)₂ solution was prepared, then 0.200g of sulfide mineral was added. The pH of the solution was adjusted by adding 0.10 mol/L NaOH and 0.10 mol/L HNO₃.

After measuring the pH, the solution was placed in a wrist shaker for 24 hours in a climate-controlled room was followed by centrifugation at 15000 r/min for 20 minutes in a temperature-controlled centrifuge at 25°C.

A 20 ml aliquot was analyzed on a Perkin-Elmer plasma II inductively coupled plasma emission spectrometer (ICP). In addition to the equilibrium concentration of La (III), the concentration of sulfur and the major cations in each of the sulfide minerals suspension were measured. Analytical values represent the average of three replicate analyses on the ICP. All samples were run in duplicate. In all cases, a mineral and a solution blank were included and adjustments were made for any adsorption onto the tube wall. Initial pH and equilibrium solution pH were determined using a combination glass electrode and an Orion 940 expandable ion meter.

Effect of pH on adsorption

Parallel sets of solutions were made up containing 125 ml of a combined solution of 10^{-3} mol/L La (NO₃)₃ and 10^{-3} mol/L Ca (NO₃)₂ (background electrolyte), and the pH was adjusted to desired value with 0.10 mol/L NaOH or 0.125 mol/L HCl. Value for pH range from a low of 2.0 to a high of 10.0. To this solution, 1.000 g of air-dry sulfide mineral was added and the suspension was shaken for 24 hours at 25°C in a climate-controlled room, then removed and centrifuged at 15000 r/min for 20 minutes at 25°C.

A 20 ml of aliquot of the supernatant was removed and the pH and E_H were measured with a combination glass electrode and a platinum electrode on an Orion 940 expandable ion meter, measuring the equilibrium concentration of the La (III), the sulfur, and the major cations present in each suspension. Appropriate solution and mineral blanks were run in certain circumstances, the pH of the equilibrium solution was increased by adding 0.10 mol/L NaOH and shaking the solution for 4 hours. This procedure was repeated until the desired pH was obtained. The mineral was dried at 100°C and weighed. This weight was used to correct the air-dry weight value.

Effect of EDTA on lanthanum sorption

A 25 ml solution of 3.92×10^{-4} mol/L EDTA was mixed 0.5ml of 10^{-4} mol/L La (III) and 0.2 g of sulfide mineral. The solution was shaken for 24 hours at 25°C, then centrifuge for 20 min. at that temperature. After centrifugation, the supernatant was analyzed by ICP.

Desorption of lanthanum

To each tube containing the La (III)-mineral complex was added 25 ml of desorbing agent (10^{-4} mol/L EDTA). The solution was put in a wrist shaker for 24 hour in a climate controlled room at 25°C. Then the tube was placed in a temperature-controlled (25°C) centrifuge and centrifuged for 20 min. at 10000 r/min. The solution was analyzed by ICP.

Calculation of partition coefficients (Kd)

The partition coefficient is defined as the amount of metal adsorbed per gram of sulfide mineral (in $\mu\text{mol/g}$) divided by the equilibrium metal concentration (in $\mu\text{mol/L}$). The units are

liters/gram. To compare La (III) adsorption on sulfide mineral as a function of treatment, an equilibrium concentration was selected and the appropriate K_d was calculated. The criteria for selection of the appropriate equilibrium concentration was that it either be a midrange equilibrium concentration or, if this was not feasible, the highest metal equilibrium concentration possible for that particular treatment.

RESULTS AND DISCUSSION

Adsorption isotherms of lanthanum

Fig. 1 shows that the experimental adsorption isotherms of lanthanum on the four sulfide minerals are conducted at near the pH of the mineral's natural acidity. A comparison between the extent to which the four sulfide minerals adsorbed La (III) was obtained by selecting a metal equilibrium concentration midway in the range and picking off the appropriate amount of metal adsorbed for each mineral. The isotherm generally indicates that the adsorption amount increases with increasing equilibrium solution concentration.

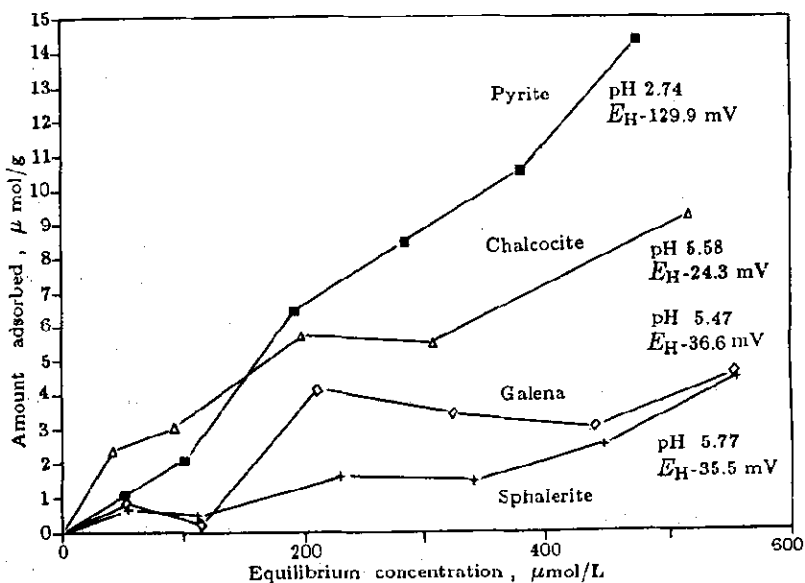


Fig. 1 Adsorption isotherms of La (III) on four sulfide minerals

The order of La (III) adsorption on sulfide minerals based on K_d is pyrite (0.03) > Chalcocite (0.02) > Galena (0.013) > Sphalerite (0.005). Pyrite's affinity for La(III) is stronger than the other minerals. From an environmental view, pyrite is an important constituent affecting the transport and transformation of lanthanum in soils, sediment, and aquifers.

The Dependence of adsorption on pH

The Fig. 2 through 4 demonstrate that adsorption of lanthanum on sulfide minerals increases dramatically with increasing solution pH and metal concentration. Pyrite has a greater

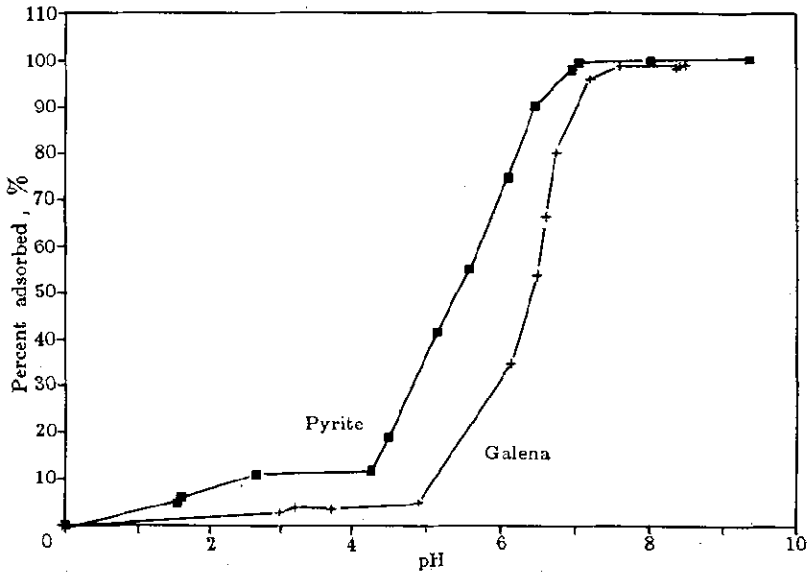


Fig. 2 The effect of pH on the adsorption of La (III) by two sulfides

affinity for La (III) than does galena, particularly in the pH range of 4.2 to 7.1. The affinities are similar to those observed by Benjamin (1979) and Benjamin and Leckie (1981) for the adsorption of heavy metals on hydrous oxide surfaces.

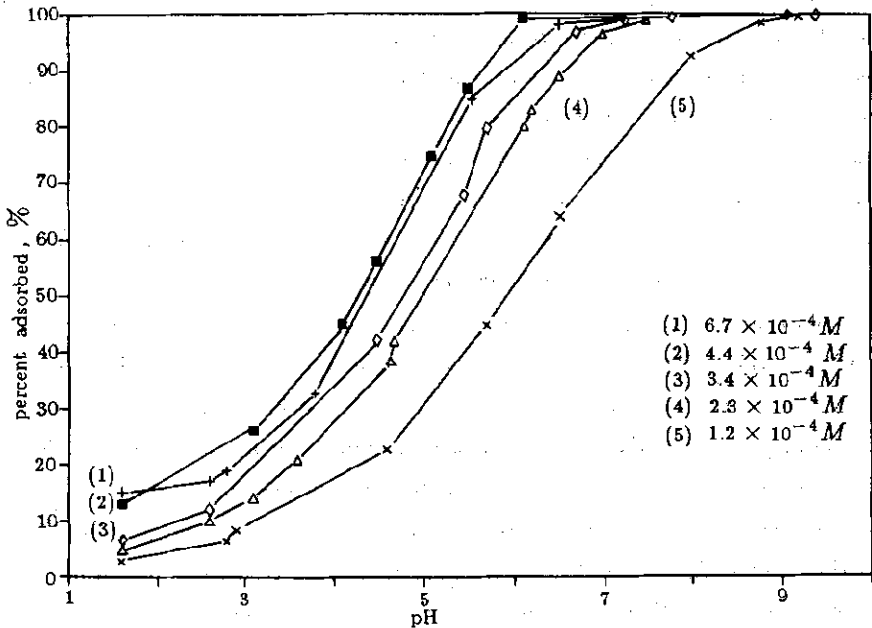


Fig. 3 The effect of pH and metal concentration on the adsorption of La (III) by pyrite

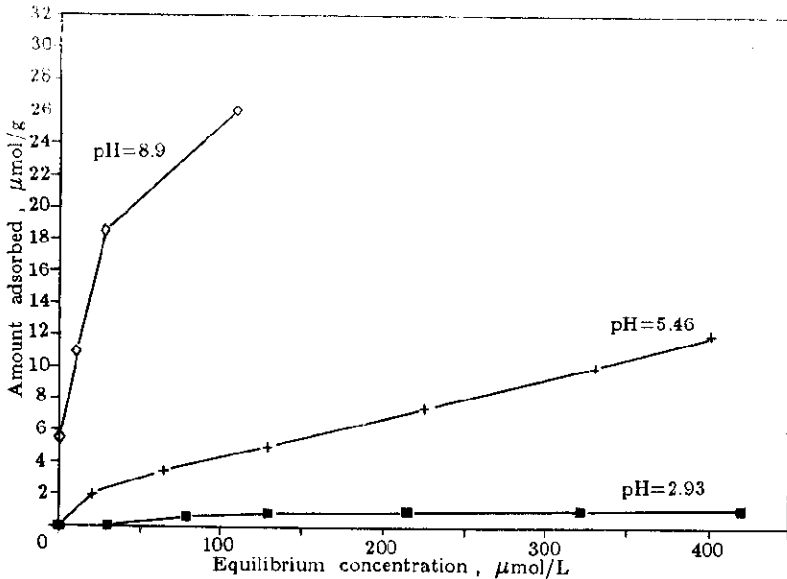


Fig. 4 Adsorption isotherms of La (III) on galena at different pHs

This S-shaped curve in Fig. 2 is called the adsorption edge and shows that complete adsorption occurs within plus or minus 1 to 2 pH unit of the established concentration. The pH_{50} is defined as the pH at which 50% of the amount of the metal added is adsorbed. Lin *et al.* (1988) determined the adsorption edge and calculated the pH_{50} for La (III) is 6.4 on galena and 5.3 on pyrite. Increases in the initial metal concentration reduce the pH_{50} value. For pyrite, pH_{50} increases from 5.3 to 6.1 as the concentration changes from 6.7×10^{-4} to 1.2×10^{-4} mol/L. Therefore, the pH_{50} value is related to the metal type and concentration and to the nature of sulfide surface. The hydrolysis constant of the metal and the intrinsic acidity constants of the sulfide mineral surface are the major contributing factors.

Fig. 5 shows that precipitation of lanthanum rarely occurs until the solution reach pH 8.2 at a concentration range of 10^{-4} mol/L. This is in line with the value of the pH 7.82 cited by Moeller (1972). A comparison of the data in Fig. 3 and Fig. 5 shows that the cause of adsorption of lanthanum on sulfide minerals is neither hydrolysis nor precipitation. We believe it to be complexation, i.e., Lewis acid and base reaction in principle.

The complexation adsorption model by Stumm *et al.* (1976) can be used to fit the data and explain the results. In this model, the hydrous oxides are treated as diprotonic acid. We also treated three of the sulfide minerals as diprotonic acid. The acid-base titration curve of galena as shown in Fig. 6. The intrinsic acidity constants illustrate that the acidity of the sulfide mineral is stronger than the hydrous oxides. The acidity constants of sulfide more closely approximate that of acetic acid. The titration curve inflection is steeper than that of the oxides.

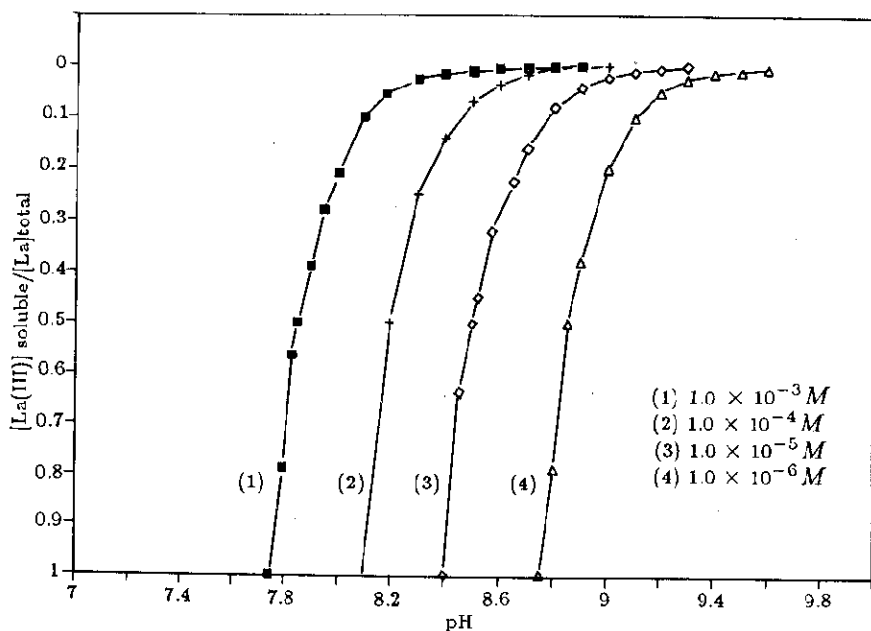


Fig. 5 Species distribution of La (III) - EDTA

Effect of ligand on the adsorption of lanthanum

The presence of an organic ligand in solution dramatically influences the adsorption characteristics of lanthanum ion to mineral surfaces. Fig.6 shows that the effect of the organic ligand (EDTA) on adsorption is very important. Comparison of Fig. 1 with Fig. 7 shows that the adsorption amount increases about five-fold to ten-fold in the presence of the complexing agent. The order of adsorption for pyrite and chalcocite in presence of EDTA is reverse to that in absence of EDTA.

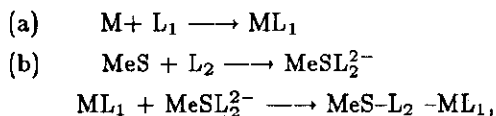
La (III) is a hard Lewis acid and EDTA is a hard Lewis base (Jensen, 1980); the two, therefore, would be expected to form a stable complex. This can be seen in Fig. 8. La (III) should bind with other carboxylate acid primarily by electrostatic interactions and little evidence exists for any covalent interactions.

Based on the stability constants of the metal complexes by EDTA, the sequence of adsorption in the presence of EDTA may be similar to the order of stability constants of the metal-EDTA complexes (the metal being the host cation present in each of sulfide minerals).

Adsorption mechanisms

Several binding mechanisms can be postulated for binding both the metal and the metal-ligand complex to the sulfide surface. These include four mechanisms proposed by Bowers and Huang (1986):

1. Metal-ligand complex bound to sulfide-ligand complex



where M=metal

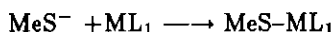
L_1 =EDTA

L_2 =another ligand like $La(OH)^{2+}$

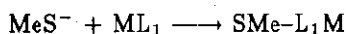
MeS^- =metal sulfide surface

Me=Host metal of the sulfide mineral

2. Metal of the metal-ligand complex bound to S-2 surface site



3. Ligand of the ligand-metal complex mineral



4. Bidentate complex

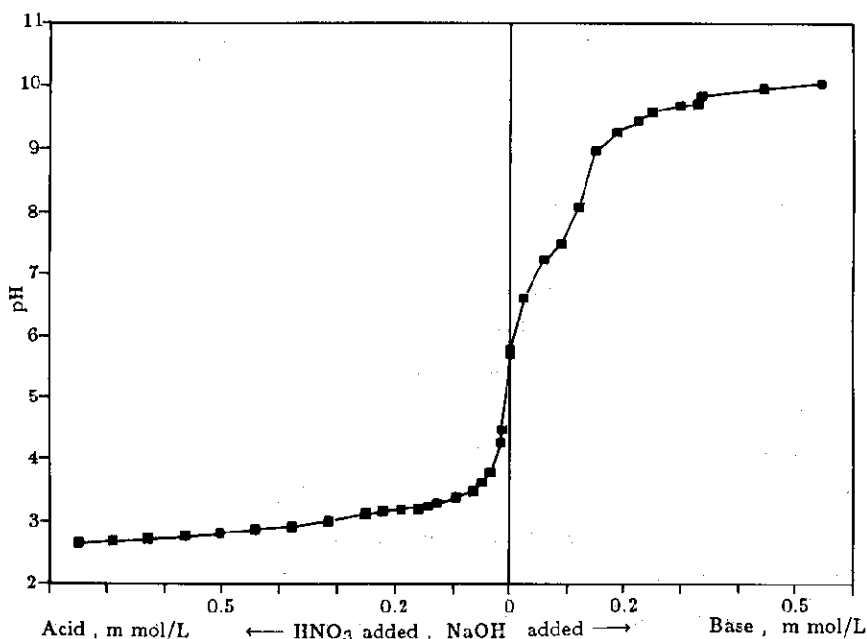
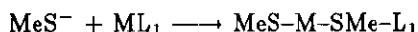


Fig. 6 The effect of pH on precipitation of La (III) at different concentrations

Stable 1:1 metal chalets can be formed between EDTA and lanthanum. Compared to the free hydrated ion with which it is in equilibrium, the metal chalet adsorbs preferentially onto the metal sulfide surface. The free hydrated trivalent ion, La(III), also may be adsorbed, but not the hydrolysis product. The soluble La (III) ion is a weak acid and not extensively

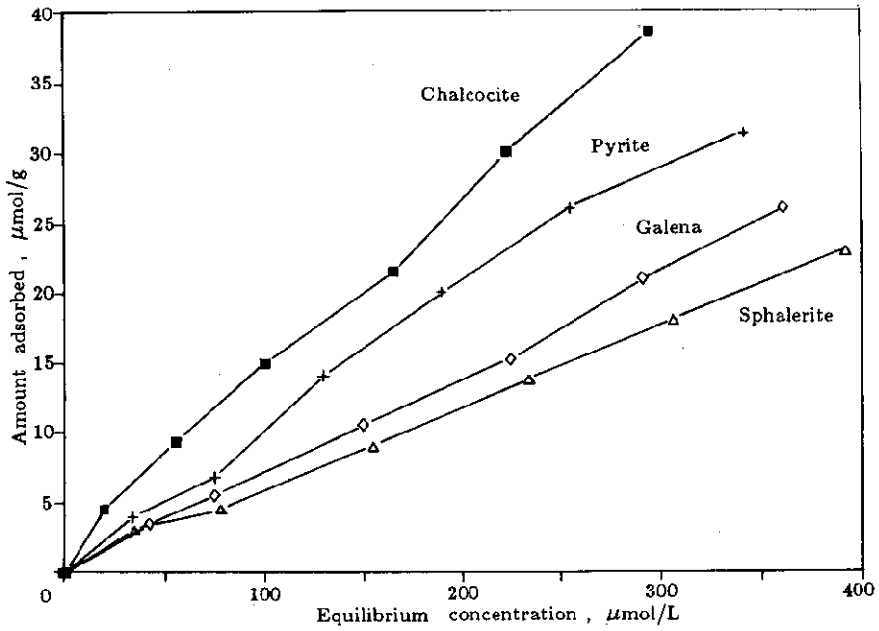


Fig. 7 The titration curve of galena

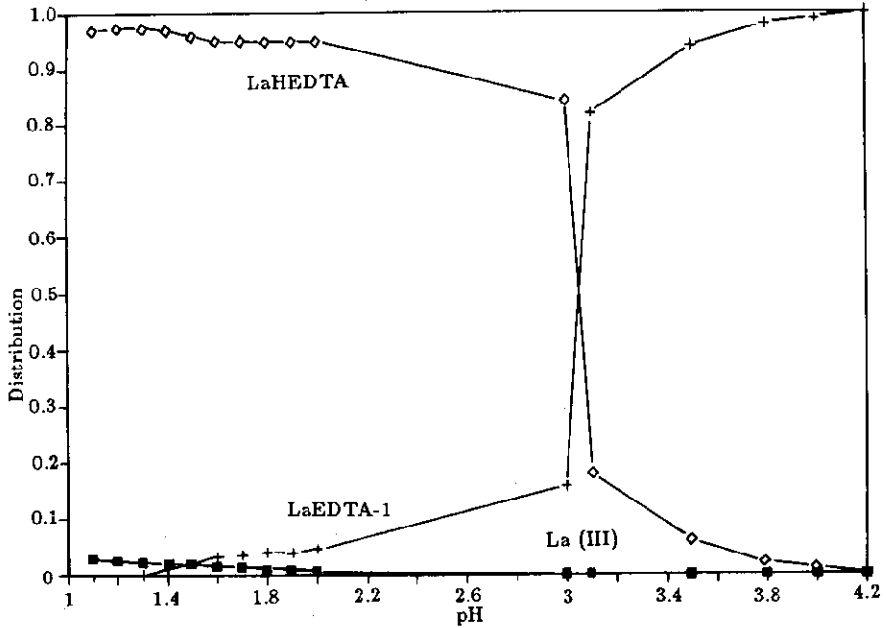


Fig. 8 Adsorption isotherms of La (III) - EDTA complexes on four sulfide minerals

hydrolyzed. A strongly basic anion like Sn^{2-} , however, produces a sufficient concentration of hydroxide ions by hydrolysis such that precipitates of basic salts or hydroxides in contact with La (III) ion are produced. The adsorption of La (III) also may be due to the presence of the organic ligand. The preference of the EDTA ligand for the various metal/metal sulfide surfaces is pyrite < sphalerite < galena < chalcocite.

La_2O_3 and $\text{La}(\text{OH})_3$ are nearly quantitatively insoluble in water, but, because of their relatively high basicity, dissolve readily in acids. These salts/hydroxides would only be present under an alkaline environment.

Stable 1:1 metal complexes with EDTA can be formed prior to the introduction of the sulfide mineral. These metal complexes can be adsorbed onto the mineral surface. The amount of lanthanum adsorbed is enhanced due to the presence of the chalet component of the metal-EDTA complex available on surface. On the other hand, the EDTA also can coordinate with the metal ion on the surface of sulfides. With the exception of Fe(II), the stability constants of EDTA-host metal on surface sites are always higher than that of EDTA-lanthanum by around 2 to 4 orders of magnitude. Ligand bridges between the surface and the lanthanum ion, as discussion above, are hypothesized.

The formation of a lanthanum sulfide mineral might be an expected reaction. La_2S_3 can be formed, but only in nonaqueous systems and at elevated temperature and is readily hydrolyzable in the presence of water. Therefore the reaction would not occur environmentally at the metal sulfide surface.

The reversal in the order of binding of Lanthanum between the two minerals may arise from the difference in the stability constants. The stability constant for EDTA-Fe(II) complex is smaller than that for the Cu(II)-EDTA. The configuration of EDTA-metal complexes at mineral surface needs to be studied in the future.

To induce the adsorption of a metal, the anion must be adsorbed to form a complexation and be capable of establishing a ligand bridge between the surface and the metal cation (Bower, 1986).

Fig. 9 shows that the pH of solution influences the adsorption of the La-EDTA complex-adsorption decreases with decreasing pH. The hydrogen ion competes with the complex very well for sorption sites on the surface the sulfide minerals. It is evident that the stable 1:1 complex of EDTA-La(III) can be adsorbed preferentially on the surface.

Desorption of lanthanum from sulfide minerals

To understand the transport characteristics of lanthanum in the environment, the desorption behavior needs to be studied. Fig. 10 shows that the desorption of La (III) reaches equilibrium in 6 hours. The desorbate equilibrium concentration is different due to the difference in the amount adsorbed on pyrite. Fig. 11 shows the relationship of the amount desorbed to the amount adsorbed. The amount desorbed increases when the amount adsorbed on pyrite increases. Desorption may reach a plateau value, however, when the adsorption amount in-

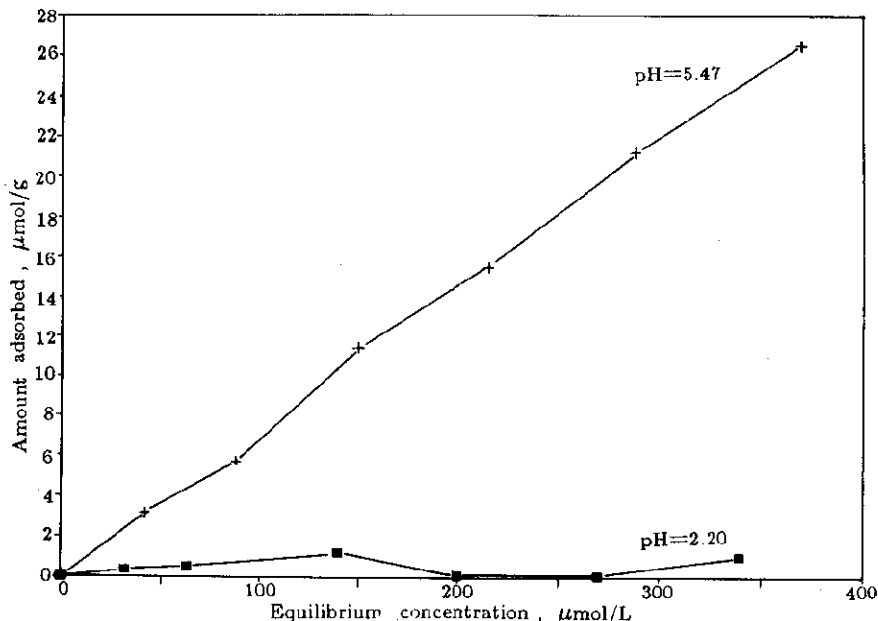


Fig. 9 Adsorption isotherms of La (III) —EDTA complexes on galena at different pHs

creases. The reason for this may be hydrolysis and precipitation of the lanthanum ion, when desorption concentration is around 1 ppm.

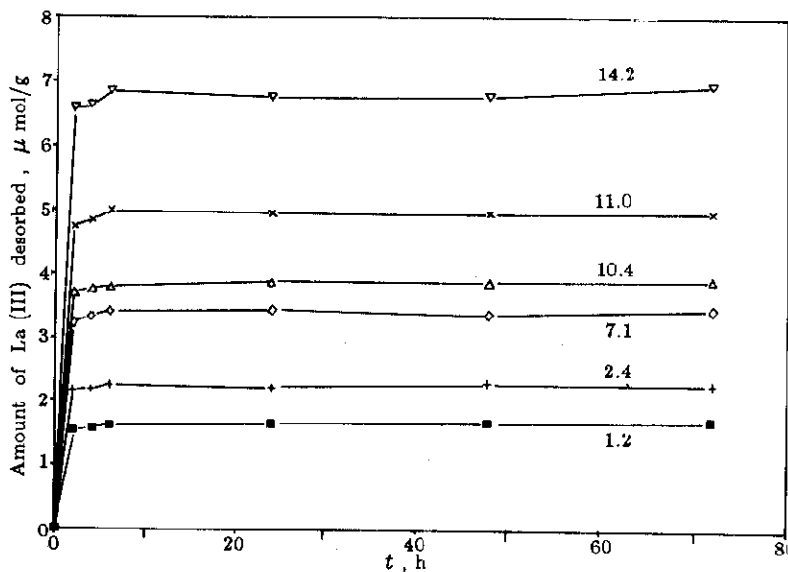


Fig. 10 The kinetics of La (III) desorption from pyrite by Ca(NO₃)₂ at different initial adsorbed metal concentrations

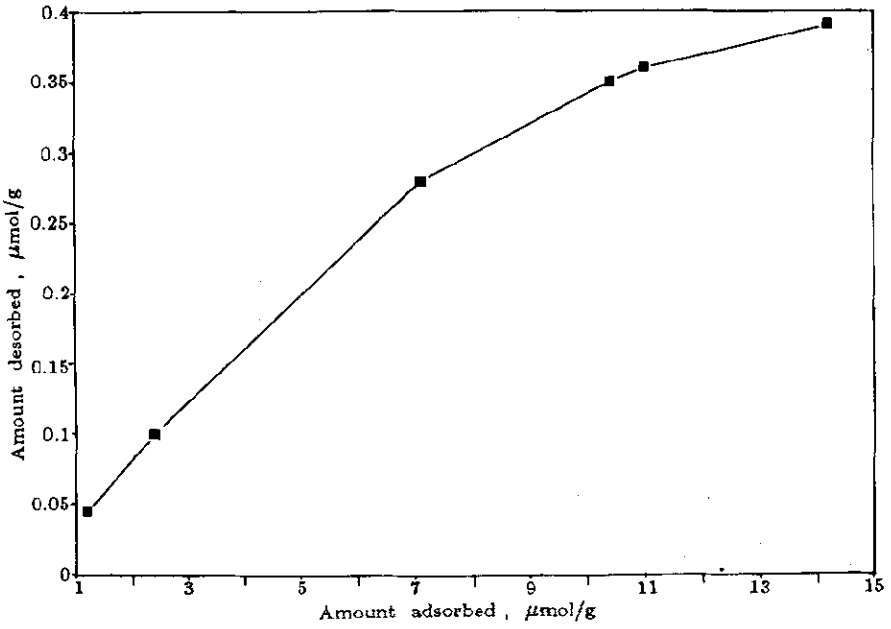


Fig. 11 The relationship between adsorption and desorption of La (III) on pyrite. (Desorbing agent was 10^{-3} mol/L $\text{Ca}(\text{NO}_3)_2$)

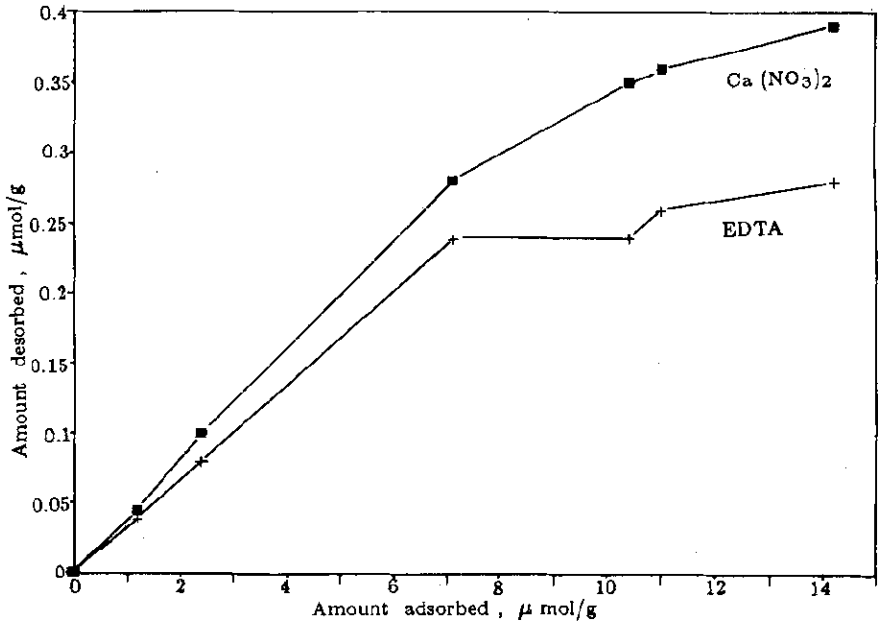


Fig. 12 The effect of desorbing agent on the release of La (III) from pyrite at pH=4.0

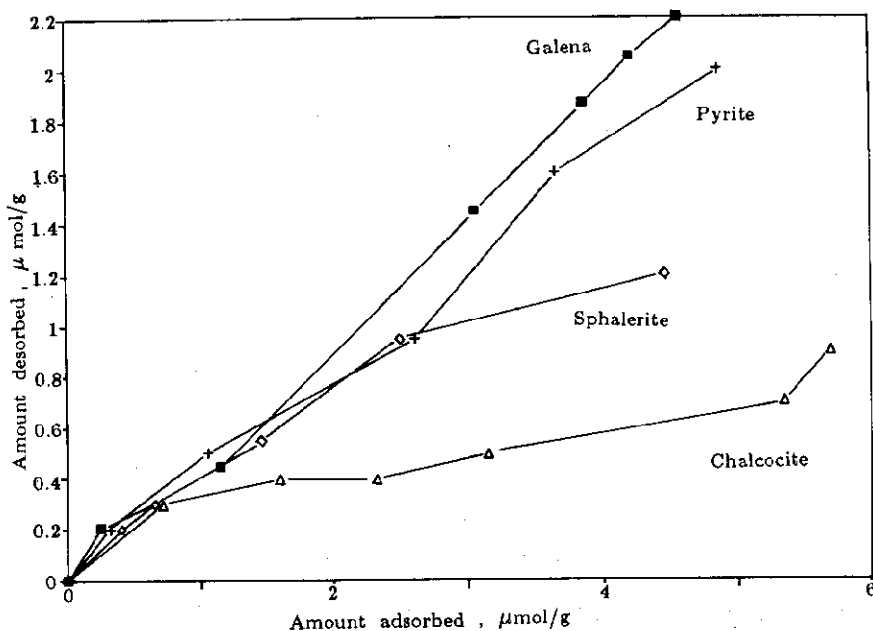


Fig. 13 The desorption of La(III) from four sulfide minerals in the absence of EDTA (10^{-3} mol/L $\text{Ca}(\text{NO}_3)_2$)

Fig. 12 compares the effect of EDTA and background electrolyte on desorption of La (III) from pyrite; the result shows that more La (III) was desorbed by the back ground electrolyte, $\text{Ca}(\text{NO}_3)_2$, than by EDTA. This phenomenon is consistent with the effect of EDTA on adsorption. The amount adsorbed increases in the presence of EDTA due to chemical complexation.

Fig. 12 and 13 show that the sequence of lanthanum adsorption on pyrite (and probably other sulfides) may play an important role in desorption of the metal. In the case of lanthanum adsorption in absence of EDTA, the desorption by EDTA is easier than that for the desorption of La-EDTA complexes on sulfide. The extent of desorption is greater by about an order of magnitude. It illustrates that the EDTA will enhance the stability of lanthanum bound on the sulfide minerals.

Fig. 14 shows that the stability of La-EDTA complexes on the sulfide minerals is different. The order of stability is sphalerite > pyrite >> galena > chalcocite (Fig. 14 and 16). Conversely, the order of stability of lanthanum on the surface in the absence of EDTA is chalcocite > sphalerite > pyrite > galena (Fig. 13 and 15).

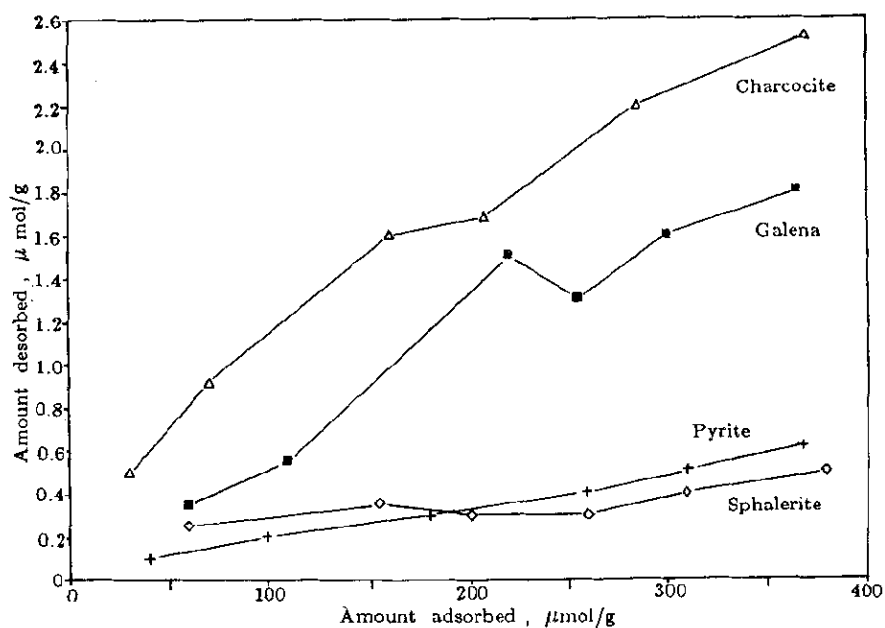


Fig. 14 Desorption of La (III)-EDTA complexes from four sulfide minerals by 10^{-3} mol/L $\text{Ca}(\text{NO}_3)_2$ at pH 4.0

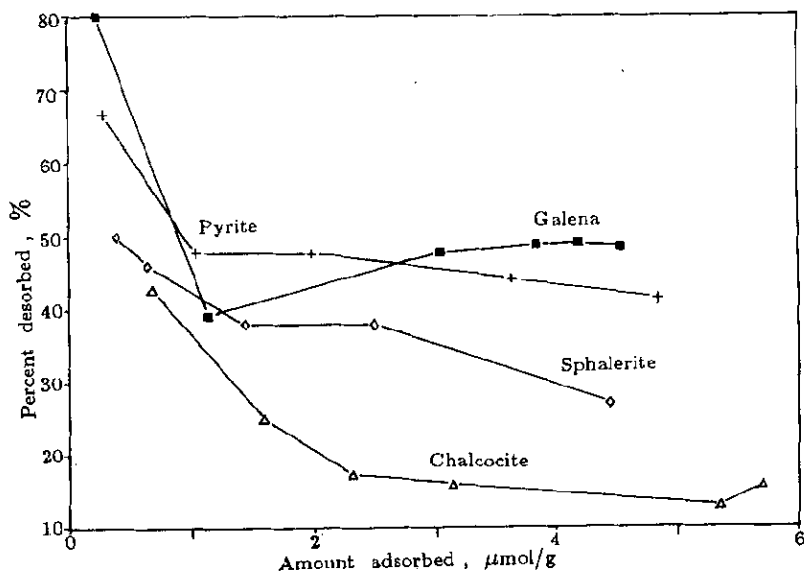


Fig.15 The percent desorption of La (III) from four sulfide minerals in the absence of EDTA. (Desorbing agent 10^{-3} mol/L $\text{Ca}(\text{NO}_3)_2$)

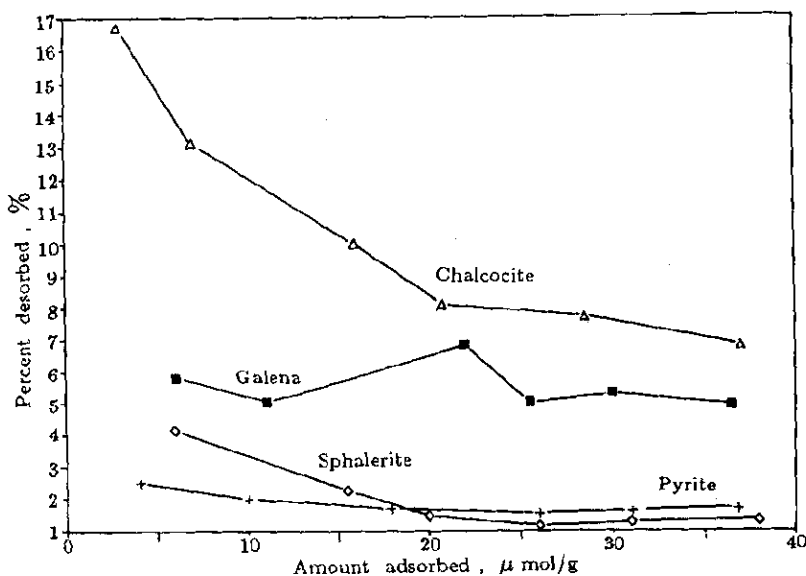


Fig. 16 The percent desorption of La (III)-EDTA complexes from four sulfide minerals after extraction with 10^{-3} mol/L $\text{Ca}(\text{NO}_3)_2$

SUMMARY AND CONCLUSIONS

The adsorption sequence of lanthanum alone on sulfide is pyrite > chalcocite > galena > sphalerite. The effect of pH on adsorption is very important. The pH_{50} of La (III) is 6.4 on galena; 5.3 on pyrite. The pH_{50} not only depends on the type of sulfide mineral, but also on the concentration of lanthanum present. The complexation mechanism explains the result.

EDTA can enhance the amount of lanthanum bound on sulfide minerals and can change the sequence of adsorption on sulfide minerals; the sequence of adsorption being chalcocite > pyrite > galena > sphalerite. The results show that the stability constant of La-EDTA complexes has a very important effect.

The adsorption configuration of the La-EDTA complex was proposed to describe the observed results. The desorption behavior of La (III) on sulfide was examined in the laboratory; on sulfide the stability of lanthanum is different from that of La-EDTA complexes. The stability of La-EDTA complexes at the surface is greater than that of the free hydrated lanthanum ion. The percent desorption of the La-EDTA complexes is an order of magnitude less than that of the lanthanum ion itself.

Sulfide minerals play an important role in the transport and transformation of lanthanum in the environment. Both pH and complexing organic ligand will influence the fate of lanthanum

in soil, sediments and aquifer materials. The presence of soluble organic ligands in soil solution or pore water and their complexation with lanthanum will decrease the mobility of lanthanum through porous media because of enhanced adsorption to sulfide minerals. In the absence of soluble organic ligand, lanthanum adsorption will increase as the pH increases, and hydrolysis and polymerization will then occur resulting in precipitation above pH 7.8.

Acknowledgments—A great deal of thanks to Dr. Jennie Ching-I Liu and Dr. Rosema C. Russo, and appreciation to Dr. A. L. Page, and Dr. Charles E. Weaver. The technical assistance of Mr. Y. Shane Yu, Mr. F. David Stees, and Ms. Laura S. Rickles is gratefully acknowledged.

REFERENCES

- Benjamin, M. M., Ph. D. Thesis, Stanford: Stanford University, 1978, 241
- Benjamin, M. M. and James O. Leckie, *J. Colloid and Inter. Sci.*, 1981, 79:209
- Bowers, A. R., and Huang, J. *Colloid and Interface Sci.*, 1986, 110:575
- Brown, D. S., R. Carlton and L. A. Mulkey, EPA/600/3-86/030. U. S. Environmental Protection Agency, Athens, GA, 1986
- Davis, J. A. and J. D. Leckie, *J. Colloid and Interface Sci.*, 1978, 67:90
- Jean, G. E. and G. M. Bancroft., *Geochem. et Cosmochimica Acta*, 1986, 50:1455
- Jellinek, F., *Inorganic Sulfur Chemistry* (Ed. by G. Nickless), Elsevier Publishing Company, New York, 1986, 670
- Jensen, W. B., *The Lewis Acid-base Concepts: An Overview*, New York: John Wiley and Sons, 1980, 364
- Kotly, S. and L. Sucha, *Handbook of Chemical Equilibria in Analytical Chemistry*, New York: John Wiley and Sons, 1985, 175
- Lin, Y., G. W. Bailey and A. T. Lynch (in publishing), U. S. EPA Research Laboratory, Athens, Georgia, 1988
- Stumm, W., Hohl, H. and F. Dufang, *Croat. Chemica Acta*, 1976, 48:491
- Travis, C. C. and E. L. Etnier, *J. of Environmental Quality*, 1981, 10:8