

The Co-precipitation Characteristics of Pb in highly Alkaline Wastewater by CO₂ Bubbling

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Abstract—The change of pH value in the wastewater, the characteristics of Carbonate precipitation and hydroxide precipitate by Pb, the adsorption and co-precipitation characteristics with the hydrated oxides of iron and aluminum and calcite have been researched by CO₂ bubbling. After CO₂ was bubbled to the high alkaline wastewater, showed the pH value of waste and the content of Pb after filtering was measured by Inductively Coupled Plasma (ICP), and then analyzed the precipitate by X-ray powder diffraction (XRD). The co-precipitation characteristics of Pb in highly alkaline waste by CO₂ bubbling was simulated by PHREEQC. The results showed that CO₂ neutralized the high alkaline waste effectively, and the content of Pb was significantly decreased. The outcome showed that the sediment mainly consisted of CaCO₃ and Pb in it. Hydroxide made in high pH value, and co-precipitation with CaCO₃ created by CO₂ continuing through into. Iron and aluminum hydroxide can adsorbent copper, but the phenomenon is not obvious because the amount of colloid is low.

Keywords—co-precipitation; adsorption; wastewater; CO₂; PHREEQC

I. INTRODUCTION

Colloid adsorption and co-precipitation are very mature technology in the method of water pollution. The results show that the sorption of Pb on iron and aluminum hydroxide has a strong effect, and heavy metal ions could form hydroxide precipitation [1-4]. The adsorption of heavy metals and co-precipitation can decrease the concentration of metals, moreover, remove some special metals in wastewater [5-7].

Carbonated technology is a new method. It can decrease the concentration of heavy metals, and fix the metals, and then decrease the toxicity. As we know, CO₂ is the main contributor for green house effect, it get more and more attention. Ca²⁺ exist in high alkaline, which is the materials for CO₂ fixed [8-11]. Because it is easy to get CO₂, so we not only solve the problem of

materials, but also treat the fixed of CO₂. Therefore, carbonated technology has a good application foreground [12.13].

II. EXPERIMENT

A. Method

X-ray diffraction(XRD) examinations on samples measurements were conducted using a X'Pert Pro diffractometer using Pb K α radiation(U=50 KeV, I=200 mA) to identify the crystal phase of the precipitates. Scans were conducted from 10° to 70° at a rate of 4° 2 θ ·min⁻¹.

Field emission scanning electron microscope-spectroscopy(SEM-EDS).

Scanning electron microscope (SEM) observations sediments using a Ultra Plus using secondary electron imaging. The resolution was 6 nm, and the voltage was 20 kV.

Field emission scanning electron microscope - energy dispersion X-ray spectroscopy (SEM-EDS) measurements were conducted to identify the mineralogical inventory and distribution of heavy metals in the sediments. The samples were covered with gold before examination and used a JSM6301 analyzer with voltage of 15 kV and 1.5 nm resolution analysis.

The wastewater was neutralized by bubbling CO₂(Table 1), and was continuously stirred using a Teflon-coated magnetic stirring bar. The pH of the solution was measured by pH meter. The generated solids were collected by filtration through membrane filters (0.45 μ m inorganic membrane). The filtrate was acidified with 10% nitric acid to a pH<2 for analysis of ions with ICP-MS. The solid materials and membrane were dried at 105 °C and then analysed by XRD. To make sure the concentration of heavy metals, reagent was added into filtrate, for example, CaO is for Ca²⁺, CuCl₂ is for Cu²⁺.

TABLE I. THE CONCENTRATION OF IONS IN ALKALINE WASTEWATER (PH:12.58 TEMPRETURE:25 °C)

Ions	Ca	Pb	Fe	Al
Con. (mg/L)	512.2	61.04	0.083	2.954
Ions	Na	K	Cl	
Con. (mg/L)	269.143	1577.606	13045.6	

B. Modeling

The mechanism of heavy metals precipitation in solution was studied by PHREEQC. The balance equation and equilibrium constants of the soluble and precipitated phases in the heavy metals were from databases in PHREEQC2.15.0 (Version 2). Geochemical equilibrium can be well simulated by PHREEQC.

III. RESULTS AND DISCUSSION

A. The results of Pb by ICP

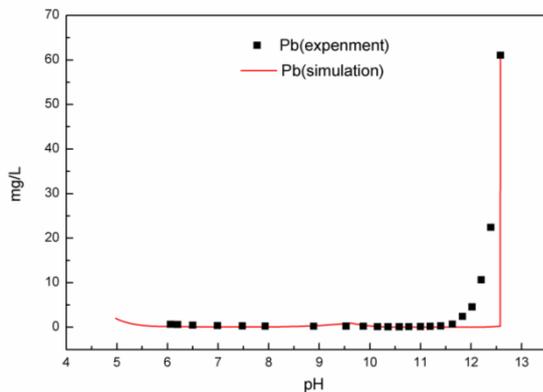


Figure 1. The change of concentration of Pb^{2+}

First stage, with CO_2 bubbling, pH value decreased from 12.58 to 11.63 and the concentration of Cu^{2+} sharply decreased from 61.04mg/L to 0.711mg/L, which reduced to 1.16% of the initial concentration. What is more, Pb^{2+} and OH^- in the solution reached maximum which generated a large amount of Pb^{2+} precipitation, and it is 2.95×10^{-4} mol/L under the pH value of 11.76.

Second stage, continued on bubbling CO_2 , pH value decreased from 11.63 to 7.9, and the concentration of Pb^{2+} slowly decreased 0.2% of the initial concentration and reached to 0.26 mg/L. In this process, most Pb^{2+} had been removed.

Hence, (a) With CO_2 bubbling constantly, pH value decreased gradually, and the concentration of OH^- was reduced, which caused the precipitation of $Pb(OH)_2$ dissolved rapidly. (b) The content of CO_3^{2-} increased, and produced a large amount of $Ca_xPb_{(1-x)}CO_3$. (c) The formation amount of $Ca_xPb_{(1-x)}CO_3$ equals to the dissolved amount of $Pb(OH)_2$.

Third stage, the content of Pb^{2+} increased slowly with the CO_2 continuously bubbling, which because CO_3^{2-} translated into HCO_3^- and $Ca_xPb_{(1-x)}CO_3$ dissolved.

B. The simulation of Pb

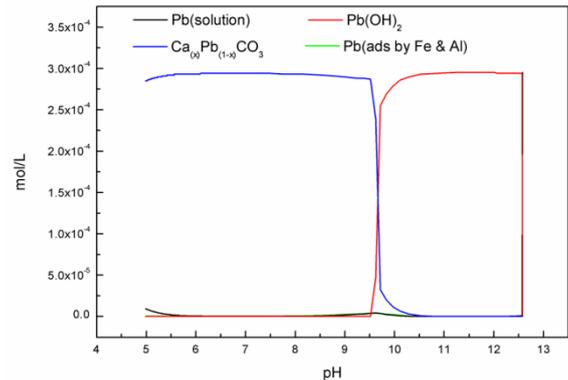


Figure 2. Concentration of all kinds of Pb in solution

First stage, when pH value decreased from 12.58 to 12.5, the content of Pb^{2+} dropped from 2.95×10^{-4} mol/L to 7.92×10^{-7} mol/L. Due to Pb^{2+} and OH^- came to the state of saturation, $Pb(OH)_2$ reached maximum in 2.94×10^{-4} mol/L. When pH value dropped from 12.5 to 10.8, almost Pb^{2+} translated into $Pb(OH)_2$, and reached maximum in 2.95×10^{-4} mol/L. When pH value decreased from 10.8 to 9.7, because $Pb(OH)_2(s)$ converted into $Ca_xPb_{(1-x)}CO_3(s)$, there was no $Pb(OH)_2$. Due to the concentration of CO_3^{2-} increased gradually and produced a large amount of $Ca_xPb_{(1-x)}CO_3(s)$, the content of $Ca_xPb_{(1-x)}CO_3(s)$ increased from 2.41×10^{-7} mol/L to 2.93×10^{-4} mol/L.

Second stage, when pH value dropped from 9.7 to 8, Pb^{2+} slowly decreased from 4.53×10^{-6} mol/L to 3.57×10^{-7} mol/L, which reduced to 0.2% of initial concentration. At the same time, $Ca_xPb_{(1-x)}CO_3$ increased from 2.39×10^{-4} mol/L to 2.94×10^{-4} mol/L, which account for 99.8% of total Pb^{2+} . The reason is for $CaCO_3$ adsorbed Pb^{2+} , and produced $Ca_xPb_{(1-x)}CO_3$. When pH value was low than 8, $Ca_xPb_{(1-x)}CO_3$ dissolved and released Pb^{2+} gradually, just because CO_3^{2-} converted into HCO_3^- and $Ca_xPb_{(1-x)}CO_3$ dissolved. From this picture, we concluded that the adsorption of $Fe(OH)_3$ and $Al(OH)_3$ can be ignored. The reason is that the concentration of Ca^{2+} is four magnitudes higher than that of Al^{3+} , and five magnitudes higher than that of Fe^{3+} , which is better than the adsorption of Fe^{3+} and Al^{3+} .

C. The analysis of XRD

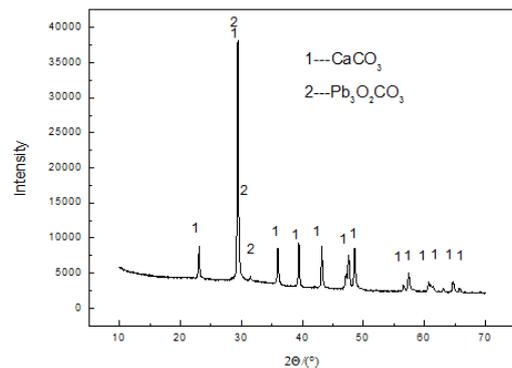


Figure 3. XRD Diffractogram at pH=6.06

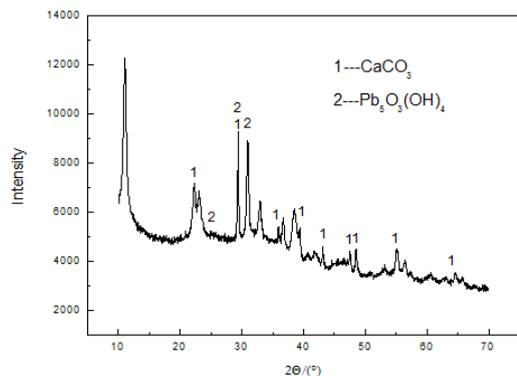


Figure 4. XRD Diffractogram at pH=12.39

Fig .3 and Fig .4 shows XRD diffractogram of the sediment at pH=6.06 and pH=12.39. At pH=6.06, the diffraction in 23、29.4、30.5、31.3、35.9、39.343.1、47.1、47.4、48.4、56.5、57.4、62.9、64.6、65.5 shows that the main component of sediment is CaCO_3 . The diffraction in 29.4、30.5、31.3 shows that the sediment containing $\text{Pb}_3\text{O}_2\text{CO}_3$. At pH=12.39, the diffraction in 23、25、29.4、35.9、39.5、43.2、47.4、48.4、50、56.5、64.6 shows that the main component is CaCO_3 and in 25、29.4、30.9 shows that the sediment containing $\text{Pb}_5\text{O}_3(\text{OH})_4$.

D. SEM-EDS analysis of the sediments

The solids generated during the co-precipitation process were evaluated using a Scanning Electron Microscope equipped with an Energy-Dispersion Spectrometer (SEM-EDS).

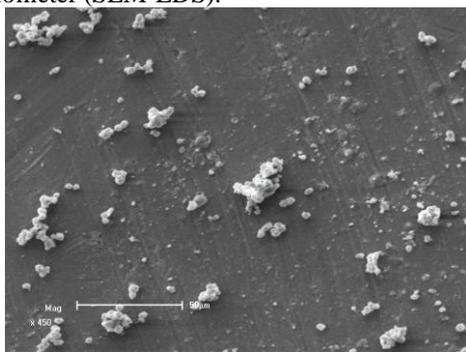


Figure 5. SEM-EDS analysis of the precipitate at pH=6.06

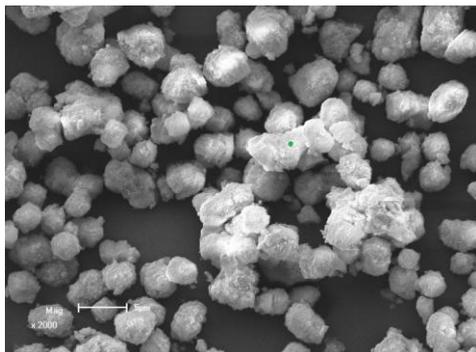


Figure 6. SEM-EDS analysis of the precipitate at pH=7.93

IV. CONCLUSIONS

From the study we it is conclude that , with CO_2 bubbling into wastewater, pH value decreased, and the concentrate of Pb was decreased significantly. With continue bubbling of CO_2 , the concentrate of Pb was increased gradually, when pH value in 6.8-7.92, the removal of Pb has a high extent, and the rate is 81.3%, which has a good removal effect.

Pb was adsorbed by Fe/Al colloid and formed co-precipitation with CaCO_3 . Due to the concentration of Ca^{2+} is four magnitudes higher than Al^{3+} , and five magnitudes higher than Fe^{3+} , so the adsorption of $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ can be ignored. The adsorption of heavy metals in wastewater by CaCO_3 was significantly better than that of Fe and Al.

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REFERENCES

- [1] Tonkin J W, Balistrieri L S, Murray J W. Modeling sorption of divalent metal cations on hydrous manganese oxides using the diffuse double layer model. *Appl[J]. Geochem.* 2004, 19: 29-53.
- [2] Csoban K, Joo P. Sorption of Cr(III) on silica and aluminum oxide: experiments and modeling[A]. *Colloids Surf.* 1999, 151: 97-112.
- [3] Zhu C. Estimation of surface precipitation constants for sorption of divalent metals onto hydrous ferric oxide and calcite[J]. *Chem.Geol.* 2002, 188:23-32.
- [4] Dixit S, Hering J G. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility[J]. *Environ. Sci. Technol.* 2003, 37: 4182-4189.
- [5] Gao, Y.& Mucci. A. Individual and competitive adsorption of phosphate and arsenate on goethite in artificial seawater[J]. *Chem.Geol.* 2003, 199: 91-109.
- [6] Giehyeon Leea, Jerry M Bighamb, et al. Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee[J]. *Applied Geochemistry.* 2002,17 :569-581.
- [7] Russell J ,Ian H Harding. Adsorption and corprecipitation of single heavy metal ions onto the hydrated oxides of iron and chromium[J]. *Langmuir* 1993, 9:3050-3056.
- [8] Namasivaym C. The adsorption of iron (III) / Cr (III) to remove cadmium with "Waste"[N]. *On geological science*, 1997.6.
- [9] Holger Ecke .Sequestration of metals in carbonated municipal solid waste incineration (MSWI) fly ash[J].*Waste Management.* 2003 ,23: 631-640.
- [10] Holger E , Nourreddine M, Anders L. Carbonation of Municipal Solid Waste Incineration Fly Ash and the Impact on Metal Mobility[J] . *Journal of Environmental Engineering* , 2003 ,129 (5) :435-440.
- [11] Majchrzak Kuceba ,Nowak W. A thermogravimetric study of the adsorption of CO_2 on zeolites synthesized from fly ash[J].*Thermochemica Acta* . 2005 ,437 : 67-74.
- [12] Vojtech Ettler. Removal of trace elements from landfill leachate by calcite precipitation[J]. *Journal of Geochemical Exploration* . 2006,88 : 28- 31.
- [13] Michael O Schwartz, Dieter Ploethner. Remove of heavy metals from mine water by carbonate precipitation in the grootfontein-omatako canal namibia[J]. *Environment Geology* 2000,39 (10) :1118-1126.