AN EFFECTIVE PROCESS FOR SIMULTANEOUS EXTRACTION OF VALUABLE METALS (V, Cr, Ti, Fe, Mn) FROM VANADIUM SLAG USING ACIDIC SODIUM CHLORATE SOLUTION UNDER WATER BATH CONDITIONS

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(Received 26 November 2017; accepted 26 February 2018)

Abstract

In the present work, a novel process for effective extraction of valuable metals (V, Cr, Ti, Mn, Fe, Al, and Mg) from the vanadium slag is proposed. The leaching parameters for valuable metals extraction from the vanadium slag by acidic sodium chlorate solution were studied to obtain conditions for vanadium to be leached without using a pyro metallurgical step since the roasting process requires high energy consumption. The optimal H2SO4 concentration, weight ratio of NaClO3 to sample, leaching time, leaching temperature, agitation speed and ratio of liquid volume to solid mass were 6 M, 0.2, 6 h, 95 °C, 200 rpm and 10, respectively. Under these optimal conditions, the extraction ratio of vanadium and valuable metals (V, Cr, Ti, Mn, Fe, Al, and Mg) were 85.8% and 91.2%, respectively. Compared with salt roasting, this process could simultaneously extract valuable metals from vanadium slag. More importantly, the experimental temperature was low underwater bath conditions.

Keywords: Valuable metals; Vanadium slag; Sodium chlorate; Water Bath

1. Introduction

Vanadium titanomagnetite ore is scattered in Australia, China, Russia, and South Africa [1]. The main pyrometallurgical processes for producing vanadium slag include shaking ladle process in South Africa [2], hot metal ladle process in New Zealand, and converter process in China and Russia [3]. In China, large amounts of vanadium slag with many valuable elements (V, Cr, Ti, Fe, and Mn) are generated annually [4]. Titanium is widely used in aircraft due to its particular properties of being lightweight, strong, and corrosion-resistant [5]. Vanadium and chromium are important alloying elements used largely in manufacturing microalloyed steel [6,7]. Manganese and iron are important elements used largely in synthesizing ferrites [8,9]. Thus, efficient utilization of such resources is of great importance.

Nowadays, the salt roasting is the main solution for vanadium extraction from vanadium slag, which includes the following procedure: salt (Na2CO3, NaCl, NaOH, Na2SO4, CaCO3 or CaO one or more mixed) roasting of vanadium slag under oxidation conditions [10-12], then water leaching of the roasted products, vanadium isolation from the leachate and vanadium precipitation [13,14], calcination precipitation, reduction of V2O5. The objective of salt roasting is to convert insoluble vanadium (III) from vanadium slag to water-soluble sodium vanadate (V) [15], meanwhile, Cr3+ converts to Cr6+ under oxidizing conditions. Although the slag roasting process increases the extraction ratio of vanadium, it consumes a large amount of energy. In today’s society, energy and the environment are major problems faced by human beings. In order to decrease energy consumption, roasting stage should be removed. Haoran et al. [16] used manganese dioxide as an oxidant to increase the acid leaching efficiency. Mirazimi [17] reported that direct acid leaching process was used to recover vanadium from LD converter slag. Li et al. [18] studied extraction of iron from vanadium slag using pressure acid leaching. Although the acid leaching process is recently researched widely, there are some problems: Vanadium slag usually contains a large amount of valuable metals (Ti, Cr, Mn, Fe, Mg, and Al) except V, which are not investigated and effectively utilized. Recently, based on principles of simultaneous extraction of iron, vanadium, manganese, chromium, and titanium from vanadium slag, novel processes, named the molten salt electrolysis, have been developed [4]. Although the molten salt electrolysis process can achieve simultaneous extraction of...
valuable metals, the temperature of molten salt electrolysis is high and the volatilization of AlCl₃ is serious.

To utilize the vanadium slag in China efficiently, an effective process for simultaneous extraction of vanadium, iron, manganese, chromium, titanium, aluminum, and magnesium from vanadium slag, using acidic sodium chlorate solution underwater bath conditions, is proposed by authors. In this process, roasting procedure was removed. The extraction ratio of valuable metals at optimal condition is high.

2. Materials and methods

2.1 Materials

Vanadium slag used in this study was obtained from Chengde Iron and Steel Company. It was crushed, dried, ground and sieved, and the sample with particle size fraction of 49-74 μm was used in this work. The sample was dried at 105 °C for 2 h and kept in a desiccator. The chemical compositions of the vanadium slag were 10.05% V₂O₃, 5.84% Cr₂O₃, 37% FeO, 20.88% SiO₂, 11.38% TiO₂, 5.93% MnO, 3.39% Al₂O₃, 3.15% MgO, 2.38% CaO. An industrial solid sodium chlorate (NaClO₃) with a purity of 99.0% was used in this work. Sulfuric acid (H₂SO₄) with analytical grades, as well as deionized water were used in this work.

2.2 Procedure

2.2.1 Acid leaching

10.0g of vanadium slag sample was usually used in this work, unless otherwise mentioned. The vanadium slag and 100 mL of 6 M sulfuric acid were added to 500 ml cylindrical plastic bottles. Then 500 mL cylindrical plastic bottle was transferred to shockbox under a gentle shock keeping at 200 rpm to obtain a mixture. The solution temperature was then raised to 40 °C for 24h. The cylindrical plastic bottle was taken out of the shockbox.

2.2.2 Water Bath

The solution in cylindrical plastic bottle was transferred to flask as shown in Figure 1. The solution temperature was then raised to 95°C using a hot water bath. Solution was agitated gently. Air was passed inside the flask by air pump. The 2.0g NaClO₃ was added to the flask at a quick rate. Meanwhile, the magnetic agitation speed was kept at 200 rpm for 6h, and then the flask reactor was taken out of the water bath. The solution was immediately filtered through a Whatman GF-A membrane with a pore diameter of 0.4 μm. The filtrate was analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, SPECTRO ARCOS EOP, SPECTRO Analytical Instruments GmbH) to measure the concentration of V. The solid residue and the membrane were dried at 105°C for 4 h, then the solid residue was removed from the membrane and weighted.

The extraction ratio of vanadium and valuable metals (Fe, Mn, V, Cr, Ti, Mg, and Al) were calculated based on equation (1-2):

\[ V_{\text{extraction}} (\%) = \frac{[V] \times V}{W_v} \times 100 \quad (1) \]

where \( W_v \) is the mass of vanadium in milligrams from the original vanadium slag; \([V]\) is the concentration of element V from the filtrate in mg/L; V is the volume of the filtrate in liter.

\[ \text{Valuable metals extraction} (\%) = \frac{W_o - W_r}{W_o \times 0.7674} \times 100 \quad (2) \]

where \( W_o \) and \( W_r \) are the weights of dried sample before and after leaching, respectively. The sum of mass percentage of oxide (FeO, V₂O₃, Cr₂O₃, MnO, TiO₂, Al₂O₃, and MgO) is 76.74.

3. Results and discussion

3.1 The possibility of reaction of various elements using acidic sodium chlorate solution underwater bath conditions

The XRD pattern in Figure 2 shows that the main crystalline phase of the original vanadium slag are fayalite, maganoan ((Fe,Mn)₂SiO₄), titomagnetite (Fe₂₋₅Ti₆₋₅O₁₄) and vuorelainite ((Mn,Fe)(V,Cr)₂O₄). Figure 3 are a backscatter electron image of an original vanadium particle and the elemental distribution image of red section by EDS, and four obvious phases can be observed. Because isomorphism widely exists in vanadium slag, the four phase can be written as ((Fe,Mn)₂SiO₄), ((Mn,Fe)(V,Cr,Ti,Mn)₂O₄), SiO₂ and CaSiO₃. Moreover, the spinel phase is randomly dispersed in the fayalite phase. Thus, the fayalite phase has to be decomposed in order to extract vanadium, chromium, and titanium. Acid leaching and oxidation by sodium
chlorate aim to destroy the structure of spinel and fayalite, then valuable metals (V, Cr, Ti, Fe, Mn) can be extracted from the vanadium slag. The chemical reactions (3-9) are as follows:

\[
\begin{align*}
2H_2SO_4 + Fe_2SiO_3 &= HS_2O_4 (colloid) + 2FeSO_4 \quad (3) \\
6Fe_2O_3 + 5NaClO_3 + 15H_2SO_4 &= 5NaClO_4 + 10(VO_2)_2SO_4 \quad (4) \\
TiO_2 + 2H_2SO_4 &= Ti(SO_4)_2 + 2H_2O \quad (5) \\
6FeO + NaClO_3 + 9H_2SO_4 &= 3Fe_2(SO_4)_3 + NaCl + 9H_2O \quad (6) \\
MnO + H_2SO_4 &= MnSO_4 + H_2O \quad (7) \\
MgO + H_2SO_4 &= MgSO_4 + H_2O \quad (8) \\
Al_2O_3 + 3H_2SO_4 &= Al_2(SO_4)_3 + 3H_2O \quad (9)
\end{align*}
\]

The effect of NaClO₃ addition on extraction ratio of vanadium and valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al) is presented in Figure 4. The vanadium extraction ratio increased from 80.7% to 92.3%, with the increase in NaClO₃ mass from 1.0 g to 4.0 g. The extraction ratio of valuable metals (V, Cr, Ti, Fe, Mn, Mg and Al) was maintained steadily in 88.3% to 92.8% across the NaClO₃ mass range from 1.0 g to 6.0 g. Assuming V₂O₃ and FeO in 10.0 g of vanadium slag completely reacted with NaClO₃ to form the corresponding compound (VO₂)_2SO₄ and Fe₂(SO₄)₃, the theoretical mass of NaClO₃ is 1.4 g. However, due to the MnO and Cr₂O₃, an excess amount of NaClO₃ should be supplied. XRD patterns of residue at 2.0 g of NaClO₃ are given in Figure 2. It was observed that the Fe₂SiO₄ disappeared and SiO₂ was produced, which could explain the fact that the extraction ratio of valuable metals was high. The scanning micrograph and EDS analysis of the residue are shown in Figure 5 and Table 1, respectively. It can be seen that the average particle size of residues are less than 20 μm. The EDS analysis of residues indicates that the content of valuable metals (V, Cr, Ti, Fe, Mn, Mg and Al) is low and the content of Si is high. Thus, valuable metals are effectively extracted. The vanadium extraction ratio decreased from 92.3% to 84.5% with the increase in NaClO₃ mass from 4.0 g to 6.0 g. The yellow sodium jarosite may wrap the vanadium slag and hinder the vanadium leaching. The chemical reaction is as following:
The element of S existed in solid leaching residue in Figure 5 and table 1, which may be attributed to form CaSO₄ and yellow sodium jarosite. Thus, decomposition of the mineral structure by sulfuric acid only is not enough, which need to join to oxidizer to promote the extraction of valuable metals.

3.3 Effect of H₂SO₄ concentration

The effect of H₂SO₄ concentration on extraction ratio of vanadium and valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al) is presented in Figure 6. The vanadium extraction ratio significantly increased with increasing H₂SO₄ concentration up to 6M, and reached to plateau at H₂SO₄ concentration range of 6-8M. The extraction ratio of valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al) increases from 63.1% to 91.2% with the H₂SO₄ concentration range of 2 M to 6M. The extraction ratio of valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al) decreases remarkably with increasing H₂SO₄ concentration from 6M to 8M. The concentration of sulfuric acid is increased to improve the concentration of hydrogen ion, promoting hydrogen ion to enter the structure of vanadium spinel and fayalite. Assuming V₂O₅, FeO, TiO₂, MnO, MgO, and Al₂O₃ in 10.0 g of vanadium slag completely reacted with H₂SO₄ to form the corresponding compound (VO₂)₂SO₄, Fe₂(SO₄)₃, Ti(SO₄)₂, MnSO₄, MgSO₄, and Al₂(SO₄)₃, the theoretical Mole of H₂SO₄ is 0.14 Mole. In our work, 0.6 mole H₂SO₄ at 6M is used for leaching valuable metals. With the sulfuric acid concentration reaching 6M, probably, the concentration of sulfuric acid is not the limiting aspect of the reaction; thus, further increasing the concentration of sulfuric acid cannot increase the extraction of vanadium. In H₂SO₄ leaching process, the reaction (3) of H₂SO₄ and Fe₂SiO₄ produces colloidal silicic acid. Colloidal silicic acid is down from solid particles with agitation of water bath. However, the viscosity of solution increases with the increase of the H₂SO₄ concentration. This is most probably due to the higher concentration of H₂SO₄, leading to reduce precipitation of colloidal silicic acid. Colloidal silicic acid deposited solid particles and inhibited the ionization of valuable metals [16]. Meanwhile, the colloidal silicic acid can absorb the positive cations of valuable metals [19]. Thus, the extraction ratio of valuable metals decreased beyond 6M. Taking into account the cost of treatment and waste acid, 6M H₂SO₄ is used for the experiment.

3.4 Effect of leaching temperature

Figure 7 shows that the effect of leaching temperature on extraction ratio of vanadium and valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al) is investigated. The extraction ratio of vanadium and valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al) are remarkably enhanced with elevating temperature. With the improvement of the water bath temperature, the movement of ions is promoted and the number of activated molecules increases. Meanwhile, the viscosity of solution with elevating temperature
decreases, which can accelerate diffusion rate of ions. Thus, hydrogen ions can more easily enter the spinel and fayalite lattice, leading to an increase in extraction ratio of valuable metals [20]. Judging from the chemical reaction rate, the reaction rate increases significantly with raising the temperature. Thus, the chemical reaction rate is controlled by the chemical reaction, because the impact of the chemical reaction with increasing temperature is far more than the impact of diffusion of ions [21].

### 3.5 Effect of time of water bath

Figure 8 presents the effect of time of water bath on extraction ratio of vanadium and valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al). The extraction ratio of vanadium increased remarkably from 50.1% to 92% with increasing time from 2 h to 10 h. The extraction ratio of valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al) increased with time up to 6 h, and then decreased slowly between 6 h to 10 h. When the extraction time is short, the reaction is not complete and the structure of spinel and fayalite cannot be destroyed. Thus, the optimal time is 6 h.

### 3.6 Effect of ratio of liquid to solid

Effect of ratio of liquid to solid (L/S) on extraction ratio of vanadium and valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al) are presented in Figure 9. The extraction ratio of vanadium and valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al) increased with increasing L/S ratio in range of 3 to 8 and reached a plateau at higher ratio than 8. However, the extraction ratio of vanadium decreases from 89.5% to 70.3% with increasing L/S ratio from 8 to 15. The extraction ratio of valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al) decreased slowly with increasing L/S ratio from 8 to 15. The moles of sulfuric acid and the concentration of oxidizing agent significantly affect the extraction rate of vanadium and valuable metals. Assuming 

\[
V_2O_3, FeO, TiO_2, MnO, MgO, \text{and } Al_2O_3 \text{ in } 10.0 \text{ g of vanadium slag completely reacted with } H_2SO_4 \text{ to form the corresponding compound } ((VO_2)_2SO_4, Fe_2(SO_4)_3, Ti(SO_4)_2, MnSO_4, MgSO_4, \text{ and } Al_2(SO_4)_3), \text{ the theoretical Mole of } H_2SO_4 \text{ is 0.14. In our work, mole of } H_2SO_4 \text{ increases from 0.18 to 0.48 with increasing at L/S ratio from 3 to 8. Generally, increasing the mole of } H_2SO_4 \text{ would increase the extraction of vanadium and valuable metals. However, this is limited by the concentration (more precisely, activity) of the oxidizing agent [19]. The concentration of the oxidizing agent with increasing ratio of liquid to solid from 8 to 15 is reduced. However, because of the separation of solution and leaching residue, it became very difficult below 10. Thus, the optimal ratio of liquid-solid is 10.}
3.7 Effect of agitation speed

As shown in Figure 10, the extraction ratio of vanadium and valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al) increased gently with increasing agitation speed from 100 rpm to 400 rpm. The reaction of sulfuric acid leaching of valuable metals is liquid-solid reaction. Stirring can reduce the thickness of the liquid film, improve the diffusion speed, and increase the extraction ratio of valuable metals. In H₂SO₄ leaching process, the reaction of H₂SO₄ and Fe₂SiO₄ produces colloidal silicic acid; meanwhile, colloidal silicic acid is down from solid particles with agitation of water bath. Vanadium slag can be more exposed to sulfuric acid. Accordingly, stirring is required.

4. Conclusions

The extraction of vanadium and valuable metals from vanadium slag using acidic sodium chlorate solution was investigated. The effects of various operation conditions on valuable metals leaching were researched. The optimal leaching temperature, leaching time, H₂SO₄ concentration, agitation speed of leaching, ratio of liquid volume to solid sample weight, time of water bath, temperature of water bath, agitation speed of water bath, adding mass of NaClO₃ were 30 °C, 24h, 6M, 200 rpm, 10 (ml/g), 6 h, 95 °C, 200 rpm and 2.0 g, respectively. Under these optimal conditions, the extraction ratio of vanadium and valuable metals (V, Cr, Ti, Mn, Fe, Al, and Mg) were 85.8% and 91.2%, respectively. Thus, extraction of valuable metals from vanadium slag was very effective and environmentally friendly with this method.

Figure 10. Effect of the agitation speed on extraction ratio of vanadium and valuable metals (V, Cr, Ti, Mn, Fe, Mg, and Al) (Acid leaching: 10.0 g of dried vanadium slag, slag particle size = 49-74 μm, 100 ml of 6M H₂SO₄, 24 h, 30 °C, 200 rpm. Water bath: 95 °C, 2.0 g NaClO₃, 6h, pump air; 200 rpm, pump air)

Acknowledgement

The financial support for the project of 51374023 from the National Natural Science Foundation of China is gratefully acknowledged.

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EFIKASAN PROCES SIMULTANÉ EKSTRAKCIJE VAŽNÍCH METALA (V, Cr, Ti, Fe, Mn) IZ VANADIJUMSKÉ ŠLJAKE KORIŠČENJEM KISELOG RASTVORA NATRIJUM HLORATA U USLOVIMA VODENÉ KUPKE

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Apstrakt

U ovom radu se predlaže novi proces za efikasnu ekstrakciju važnih metala (V, Cr, Ti, Mn, Fe, Al i Mg) iz vanadijumské šljake. Analizirani su parametri luženja za ekstrakciju metala iz vanadijumské šljake korišćenjem kiselog rastvora natrijum hlorata da bi se postigli uslovi kada je moguće lužiti vanadijum bez upotrebe pirometalurškog koraka, pošto proces prženja zahteva veliku potrošnju energije. Optimalna koncentracija H₂SO₄, odnos težine NaClO₃ prema uzorku, vreme luženja, temperatura luženja, brzina agitacije i odnos zapremine tečnosti u odnosu na čvrstu masu bili su pojedinačno 6 M, 0.2, 6 h, 95 °C, 200 rpm i 10. Pod ovim optimalnim uslovima, razmera ekstrakcije vanadijuma i važnih metala (V, Cr, Ti, Mn, Fe, Al i Mg) bila je pojedinačno 85.8% i 91.2%. U poređenju sa prženjem soli, ovim procesom bi mogla simultano da se vrši ekstrakcija važnih metala. Što je još važnije, eksperimentalna temperatura u uslovima vodene kupke je bila niska.

Ključne reči: Važni metali; Vanadijumská šlúka; Natrijum hlorat; Vodena kupka