Recovery of Vanadium from Esfahan Steel Company Steel Slag; Optimizing of Roasting and Leaching Parameters

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Abstract

In this Study, vanadium recovery from the steelmaking converter slag was studied. Salt roasting-basic leaching is the process which was applied to separate and extract vanadium from steel making slag. Ground slag was roasted after mixing with determined quantities of sodium carbonate. The effect of time and temperature of roasting and sodium carbonate content were studied. The optimum temperature, time and sodium carbonate content in the roasting process were found to be $1000°C$, 45 min and 10%, respectively.

Temperature, time, leachant concentration and particle size were optimized for leaching process. It was determined that sodium carbonate is the major leaching agent in comparison with sodium hydroxide. The most suitable conditions for leaching process was found to be $80°C$, 60 min, sodium carbonate to sodium hydroxide mass ratio of 40-50:10 and particle size between 100 and 120 mesh. More than 80% of vanadium was recovered under optimum conditions.

Keywords: Vanadium, Steelmaking slag, Recovery, Leaching.

Introduction

Vanadium has many and continuously increasing industrial uses. Today over 85% of the production of vanadium is consumed in carbon steel and stainless steel production, and production of ferro-vanadium[1].

The fly ashes produced from the combustion of heavy oils, spent catalysts used in the manufacture of sulphuric acid, slags obtained from the processing of iron ores, such as flushing slag formed during electric arc melting of a sponge iron, plus scarp charge and steelmaking converter slag are known as secondary raw materials of vanadium[2-4]. Because of lack of primary sources of vanadium and disposal of these industrial wastes which may lead to environmental problems, the processing of industrial wastes containing this element often becomes an absolute essential[5,6]. Steelmaking converter slag has become an important secondary raw material and this vanadium bearing slag is of great interest for the recovery of vanadium[7]. Vanadium, during refining of hot metal with oxygen, oxidizes and gradually becomes part of the converter slag[7-8]. Several investigations have been carried out to study the recovery of vanadium from steelmaking slag. Among the different pyro-hydrometallurgical processes used or suggested, the most widely applied one is the alkaline roasting with NaCl or Na_2CO_3, followed by water, acid and alkaline leaching[9-12]. Acid leaching is used in order to solve vanadium from the roasted materials which are present as water insoluble compounds such as calcium, magnesium and iron vanadate. Although this method is effective, the obtained solution from the leaching process is showed to have a lot of impurities which cause some problems in the later precipitation process for recovery of vanadium in the form of vanadate salts. In most cases, a carbonate bearing material such as sodium carbonate and sodium bicarbonate have been used for recovery of vanadium from roasted converter slag[12]. Chen et al. have investigated the recovery of vanadium from high calcium converter slag by mixing the slag with soda and then leaching the roasted material with sodium carbonate or bicarbonate solutions[11].

In general, high levels of free lime in converter slag, (up to 60 weight percent), has limited applying hydrometallurgical process to extract vanadium because of the high acid consumption[9]. To cope with this limitation, prior to leaching of the slags, a pyrometallurgical step has been developed in order to convert free CaO to $CaSO_4$ by roasting the slags under a SO_2-O_2 rich atmosphere. In this process,

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converter slag, after mixing with sources of SO_2 generation, was leached with sulphuric acid[9,12]. Leaching solutions are required to be purified before vanadium extraction since iron values present in solution contaminate the red cake. In an investigation by Wilkomrisky et al[9], roasting of the slag mixed with an equal weight of pyrite has been carried out at 680°C for 5 hours. They have claimed that under these conditions, vanadium recovery from converter slag becomes optimum. Also sodium phosphate has been suggested as an alternative reagent instead of pyrite which causes the formation of calcium phosphate[12]. Direct oxidizing of slag with pure oxygen is another way to convert vanadium compounds in slag to V^{+5} [9]. Vanadium compounds in the roasted slag are found to be sodium vanadate, calcium metavanadate, sodium-calcium vanadate and calcium vanadotitanate. The recovery of vanadium from roasted steel slag by sodium salts, which have high calcium contents, through leaching with water is showed to be rather low. The principal reactions involved during leaching could be the dissolution of sodium and calcium vanadate compounds if the roasted converter slag is leached with carbonate solutions. Calcium vanadate is converted to calcium carbonate via this reaction and vanadium enters the solution[11].

In Esfahan Steel Company, about 40000 tons of slag is produced annually. Due to high amounts of vanadium in this slag, 2-3% V_2O_5, recovery of vanadium seems to be necessary.

In the present investigation, an attempt has been made for the recovery of vanadium. The conditions of salt roasting and basic leaching processes have been optimized for the extraction of vanadium from this slag.

Experimental procedure

The converter slag was obtained from Esfahan Steel Company. Roasting experiments were carried out using commercial grade Na_2CO_3 powder. The ground converter slag after mixing with determined values of sodium carbonate and pelletizing, was roasted in an electric muffle furnace. Pelletizing is carried out on a rotating disc. The size of the pellets is usually between 5 to 20 mm. Roasting experiments were carried out at different roasting time, roasting temperature, and slag to Na_2CO_3 ratios. After optimizing the roasting parameters, the roasted slag at these optimum conditions was ground to different particle sizes for leaching experiments. In the leaching process, the effect of leaching time, leaching temperature, type and concentration of leachant and particle size have been investigated. Sodium hydroxide and sodium carbonate were used as leachants. X-ray diffraction method was employed for phase determination in the samples. Vanadium containing solutions were analyzed using spectrophotometery method. Chemical composition of converter slag was analyzed using XRF method.

Results and discussion
1- Slag specification

Chemical composition of the slag is indicated in Table 1. X-ray diffraction pattern of the slag and the major phases in this slag are shown in Figure 1. The main phases in converter slag are calcium hydroxide, calcium-iron oxide and calcium-silicon oxide. This is in agreement with the results obtained by Preblinger et al.[8]. Free lime which is present in converter slag, is converted to the $Ca(OH)_2$ because of the moisture in the environment.

Table 1. XRF results of chemical composition of the converter slag.

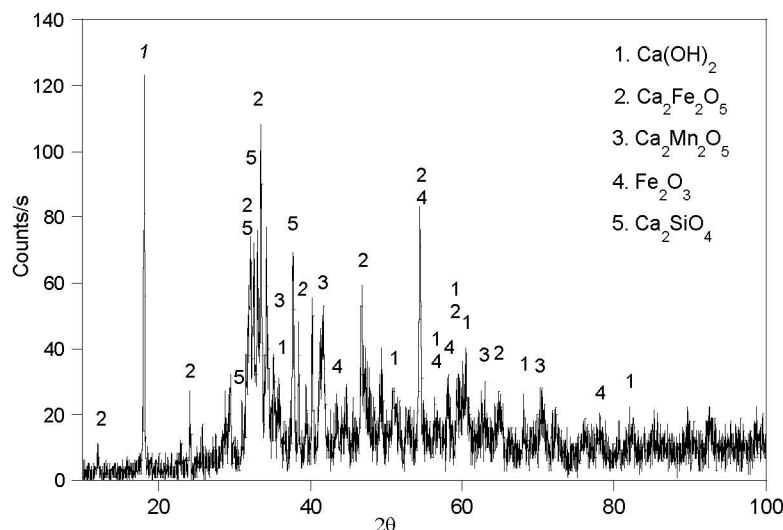| Constituent (%Wt)	CaO	Fe_2O_3	MnO	Al_2O_3	SiO_2	V	P_2O_5	TiO_2
	53.74	20.95	9.3	1	8.39	.948	2.078	1.261

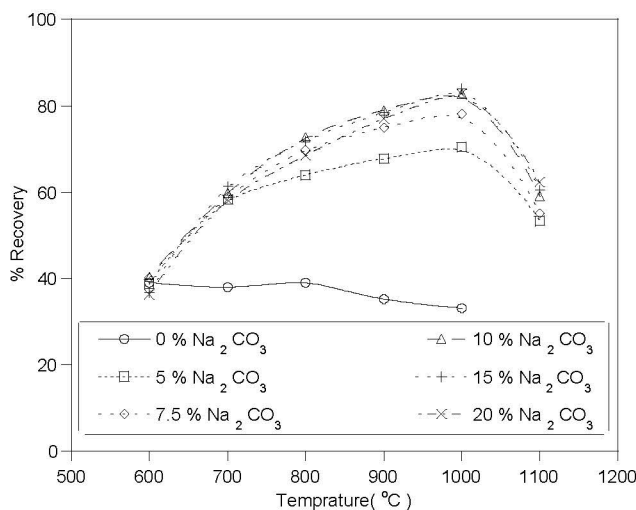*Fig. 1. X- ray diffraction pattern of the converter slag.*

Fig. 2. Variation of recovery with roasting temperature at different concentrations of sodium carbonate (Experimental conditions: roasting time 1h, leaching time 3 hours, leaching temperature 80°C and particle size 100 to 120 mesh at solid/liquid ratio: 0.05).
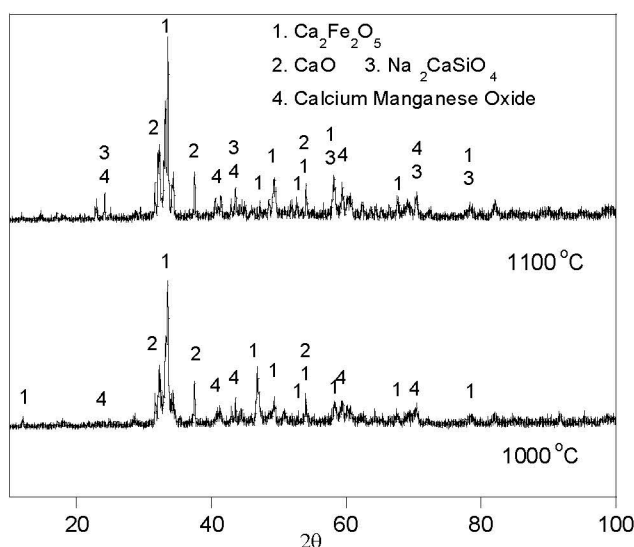

Fig. 3. X-ray diffraction pattern of the roasted converter slag at 1000 and 1100°C. (Experimental conditions: roasting time: 1h, sodium carbonate: 10 percent)

2- Effect of the roasting temperature and sodium carbonate

The effect of sodium carbonate concentration on the recovery of vanadium has been studied within a range of 0 to 20% at temperatures from 600 to 1100°C. When the amount of sodium carbonate is 0%, recovery of vanadium is very low. Indeed, the role of sodium carbonate during the roasting process is to convert calcium vanadates to sodium vanadates. From Figure 2, it can be seen that roasting temperature has an important influence on vanadium recovery. Approximately, 83% recovery of vanadium was obtained by using 10% sodium carbonate in the charge at 1000°C for one hour. Also, it is observed that at temperatures above 1000°C, the vanadium recovery dropped to 53%. The decrease in vanadium

recovery above 1000°C could be due to the formation of a glassy complex phase; namely, Na_2CaSiO_4, which is insoluble. The analysis of the X-ray diffraction pattern of the roasted slag mixed with 10% of sodium carbonate is shown in Figure 3. The results showed that at temperatures above 1000°C, a glassy phase is formed.

3- Effect of roasting time

The effect of roasting time on the recovery of vanadium was investigated at 1000°C. As shown in Figure 4, increase in the roasting time does not have any considerable effect on vanadium recovery after 45 min. During the first 45 min, calcium vanadates gradually convert to sodium vanadates, and therefore vanadium recovery increases. Therefore, based on

the results obtained, optimum roasting conditions for maximum vanadium recovery are as follows: sodium carbonate 10 percent, roasting temperature 1000°C, roasting time 45 min.
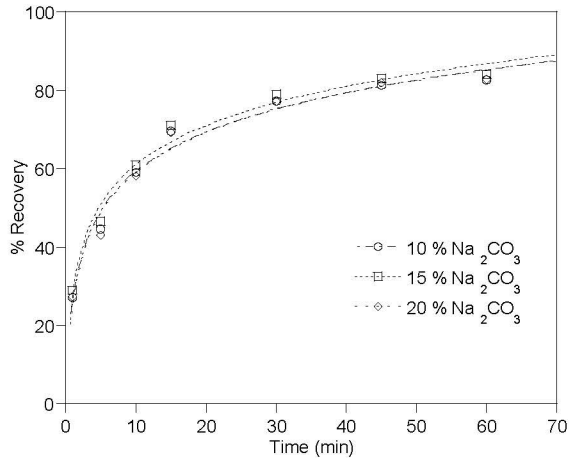

Fig. 4. The influence of the roasting time at different concentrations of sodium carbonate (Experimental conditions: roasting temperature: 1000°C, leaching time: 3 hours, leaching temperature: 80°C, particle size: 100 to 120 mesh at solid /liquid ratio: 0.05).

4- Effect of the concentration of leachants
4-1- Sodium carbonate and sodium hydroxide

The roasted slag at optimum roasting conditions was leached in sodium carbonate and sodium hydroxide solutions. The leaching time and temperature, particle size of the roasted charge, and solid/liquid ratio were 80°C and 3 hours, 100 to 120 mesh and 0.05, respectively. The effect of sodium carbonate and sodium hydroxide concentrations on the recovery of vanadium as the leachants are shown in Figure 5. It can be seen that by increasing the concentration of both leachants, the vanadium recovery will be enhanced. For all concentrations, sodium carbonate shows better performance as a leachant than sodium hydroxide. By utilizing sodium carbonate solution with a concentration between 40-50 (g/L), recovery of vanadium goes to 75%, while maximum vanadium recovery is 35% for a 70 (g/L) sodium hydroxide solution. Higher concentration of sodium carbonate causes more conversion of calcium vanadates to calcium carbonate.

4-2- Binary solution of sodium carbonate and sodium hydroxide

Figure 6 illustrates the influence of solutions containing sodium carbonate and sodium hydroxide in the leaching process of roasted slag. For all concentrations of sodium carbonate, addition of sodium hydroxide up to 10 (g/L) improves vanadium recovery and more than this amount has a negative effect. This behavior may be due to an increase in calcium ion solubility with an increase in pH and/or lowering carbonate ion activity in the solution.

According to the obtained results, it can be concluded that a solution containing $NaOH-Na_2CO_3$ with a concentration of 40-50 and 10 (g/l) respectively, had the best result. With this ratio, vanadium recovery will be enhanced up to 83%.
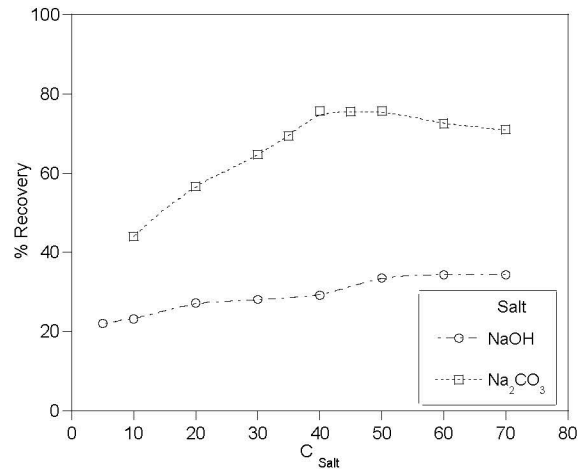

Fig. 5. The effect of leaching agents concentrate on the vanadium recovery (Experimental conditions: leaching time 3 hours, leaching temperature 80°C, particle size 100 to 120 mesh at solid/liquid ratio: 0.05).
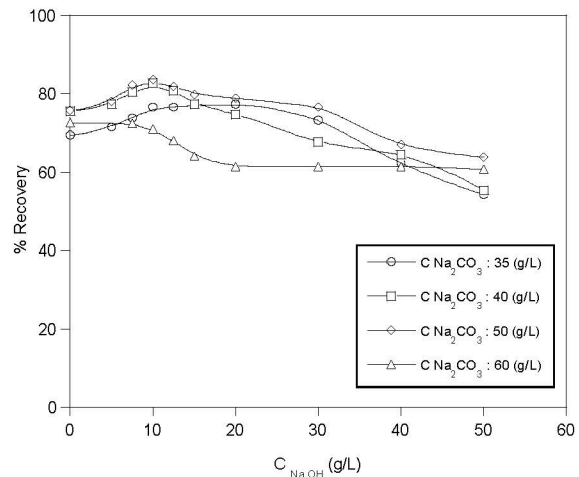

Fig. 6. The effect of the concentration of leaching agent on the recovery of vanadium (Experimental conditions: leaching time 3h, leaching temperature 80°C, particle size 100 to 120 mesh, s/l ratio: 0.05).

5- Effect of the leaching time and temperature

Experiments were carried out by varying the time of leaching from 5 min to 180 min. Leaching solution contained the 40 (g/l) Na_2CO_3 and 10 (g/l) NaOH. The recovery of vanadium vs. leaching temperature is shown in Figure 7.

The amount of vanadium recovery increases at elevated temperatures. At low temperatures, the dissolution reaction of vanadium reaches equilibrium after 120 min and vanadium recovery becomes approximately constant. Recovery of vanadium increased from 60% at 60°C to 83% at 80°C. At elevated temperatures, the recovery of vanadium

approached a constant value after 60 min. Also at these temperatures, the rate of dissolution of vanadium is more rapid in comparison to the rate dissolution at low temperatures.
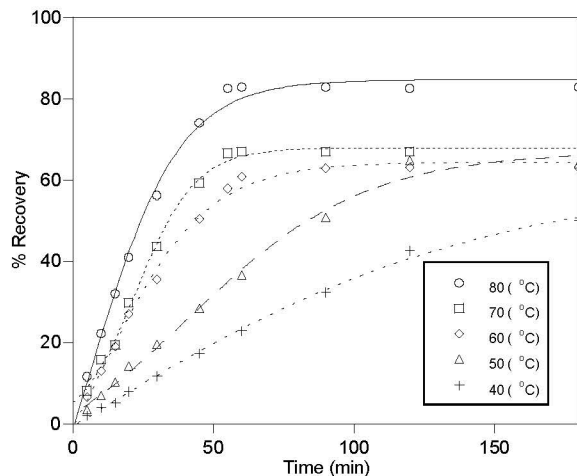

Fig. 7. The effect of the leaching temperature on the vanadium recovery. (Experimental conditions: leaching Solution: 40 (g/L) Na$_2$CO$_3$-10 (g/L) NaOH, particle size 100 to 120 mesh, solid/liquid ratio: 0.05)

6- Effect of the particle size

The effect of particle size on the recovery of vanadium is illustrated in Figure 8. Also, the obtained results, while the particle size was 100 to 120 mesh, are shown in this figure. Similar to previous experiment, there was a concentration of Na$_2$CO$_3$ and NaOH in leaching solution 40 (g/L) and 10 (g/L), respectively. Curves of Fig 8 reveal that calcines particle size has a significant effect on vanadium recovery. As a result, optimum particle size for calcines in this study was 100 to 120 mesh.
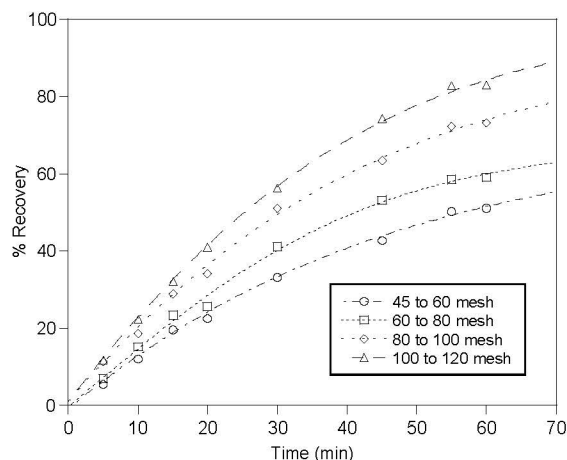

Fig. 8. Vanadium recovery as a function of the calcines particle size (Experimental conditions: leaching solution: 40(g/L) Na$_2$CO$_3$-10 (g/L) NaOH, leaching time 1h, leaching temperature 80°C, s/l ratio: 0.05).

Based on the above results, optimum leaching conditions are 80°C, 1 hour, 40-50(g/L), and 10(g/L) for temperature, leaching time, sodium carbonate and sodium hydroxide concentration, respectively.

Conclusion

1- Recovery of vanadium from a steel making converter slag produced at Esfahan Steel Company can be carried out using salt roasting-basic leaching of the converter slag.
2- Optimum conditions for vanadium recovery from this slag by sodium carbonate roasting were 10 percent Na$_2$CO$_3$ in the charge and roasting for 45 min at 1000°C, followed by leaching in solution containing 40-50 (g/L) Na$_2$CO$_3$-10 (g/L) NaOH for 1 hour at 80°C.
3- It was found that at roasting temperatures higher than 1000°C, Na$_2$CaSiO$_4$, a glassy phase, was formed and led to a decrease in vanadium recovery.
4- Particle size of the roasted slag has a significant effect on vanadium recovery.
5- Over 80 percent of vanadium present in converter slag entered the solution by optimizing roasting and leaching parameters.

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