Mechanisms Involved in the Roasting of Pellets Composed of Stainless Steel Slag and Sodium Hydroxide to Extract Chromium

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In order to extract the chromium from stainless steel (SSL) slag, the thermochemical processes involved in the roasting of pellets composed of SSL slag and sodium hydroxide were studied. It was found that Ca₃Mg(SiO₄)₂, Ca₂SiO₄, MgCr₂O₄ and MgO are the main phases from the SSL slag. Most of chromium from the slag was present in spinel phase (MgCr₂O₄). In addition, the chromium was also found in metallic phase (Fe–Cr) and periclase phase (MgO). These three Cr-containing phases were embedded in the silicate phases. During the pellet roasting, the silicate phases were destroyed by liquid NaOH and the low valence of insoluble chromium species such as MgCr₂O₄ were converted to Na₃CrO₄ at 500–700°C and CaCrO₃ at 800°C, respectively. Both were soluble in hot water. The residual chromium was only present in Cr–Fe–O phases. Many cavities were left on the pellet surface during the roasting, which facilitated the diffusion of both air and liquid NaOH. A high chromium extraction was achieved only when liquid NaOH had diffused into the cores of slag particles over 400°C.

KEY WORDS: chromium extraction; stainless steel slags; mechanisms; pellet roasting; sodium hydroxide.

1. Introduction

1.1. Background

Approximately one ton of stainless steel slag (SSL slag) is generated when producing three tons of stainless steel.1) The chromium contents in the SSL slag usually vary from 2 to 10 wt.%.2) The chromium oxide from SSL slag usually elutes as a toxic hexavalent chromium ion (Cr⁶⁺) into water due to the atmospheric oxidation of insoluble trivalent chromium to soluble hexavalent chromium.3–5) Preventing toxic Cr⁶⁺ from being eluted from the stainless steel (SSL) slag is still an unsolved problem so far in the world.6) The extraction of chromium from SSL slag might solve the environmental problem ultimately. If the Cr content left in the treated residue is lower than 0.05 wt.%, this residue can be safely disposed of in environment in China.

1.2. Preliminary Study

The conventional industrial hydrometallurgical process in chromium extraction from chromite involves adding Na₂CO₃ to chromite during the chromite roasting at 1200°C.7) We found that if a similar process was used to extract chromium from stainless steel slag, the chromium extraction was low. However, if NaOH was used instead of Na₂CO₃, the chromium extraction was increased a lot. To investigate the discrepancy in Cr extraction, the mechanisms involved in the roasting of NaOH-added pellet of SSL slag was studied in this work. Few studies have been reported to extract Cr from SSL slag by alkali roasting with NaOH so far. The thermochemical processes involved in the chromium extraction were also not investigated. Moreover, we found that the roasted powder samples tend to stick severely on the alumina crucible when NaOH instead of Na₂CO₃ is used in alkali roasting. We found that this problem can be well solved by using pellet sample instead of powder sample. Thus pellet samples were mainly used in this work. At present, some large multiple hearth furnaces and rotary kilns are being used in metallurgical industry for the vanadium slag roasting in order to extract vanadium from the vanadium slags. Probably these roasting devices can be used directly by the present process of chromium extraction. This will avoid the investment of new equipment. Thus this process has the great potential to be applied in many industries related to chromium resources.

2. Experimental Procedures

2.1. Materials

About 50 kg of SSL slag from one steel-making plant of China was used in this work. The slag has been previously processed to extract iron. The slag was crushed, dried and sieved. Unless otherwise specified, the sample with a size fraction of 58–75 μm was used in the experiments. The chemical compositions of the slag were shown in Table 1. The content of chromium calculated as Cr₂O₃ was 3.93 wt.%.
deionized water was added into a powder mixture composed of about 2.20 g of the SSL slag (58–75 μm) and about 1.32 g of solid NaOH in most of cases unless otherwise specified. The mixture thus obtained was pressed into a cylinder pellet with a diameter of 15 mm and a height of 10 mm. This pellet was placed in a corundum crucible of 30 mL. The crucible was then put in a Muffle already set at a temperature of 400–850°C. The sample was kept at this temperature for some time. After that, the crucible was taken out from the Muffle and cooled to the room temperature. The interior room of the Muffle was connected to outside air in many places such as the jack of the thermocouple. In addition, the door of the Muffle was slightly opened during the roasting process. Thus the sample was basically exposed to the atmosphere with a partial pressure of oxygen of 0.21 atm. Then the crucible with the content was placed in a glass beaker of 250 mL. About 100 mL of deionized water was added to the beaker to immerse the crucible. The water in the beaker was raised to 90°C for 5 minutes by a heating plate. In this way, the content of the crucible could be taken out completely and transferred into water in the beaker. When the mixture solution was cooled to room temperature, it was filtered through a Whatman GF-A membrane with a pore diameter of 0.4 μm. The filtrate was then put in a Muffle already set at 105°C for 4 h. Then the solid leaching residue was removed from the membrane and weighed. The percentage of extracted chromium was calculated on the basis of the following:

\[
\text{Cr extraction (\%) = } \frac{[\text{Cr}]}{W_{\text{Cr}}} \times 100 \ \ \ \ \ \ \ \ (1)
\]

where \(W_{\text{Cr}}\) was the weight of chromium in milligrams from the sample, \([\text{Cr}]\) the concentration of chromium from the filtrate in milligrams per liter, and \(V\) the volume of the filtrate in liters.

### 2.3. Chemical Analysis and Characterization

Apart from chromium, the contents of the other elements from the SSL slags were determined by X-ray florescence Spectrometer (XRF-1800, Shimadzu). The chromium contents in the slags and the leaching residues were analyzed in the following procedure. About 0.5 g of slag or solid residue was mixed well with 3 g of sodium peroxide and put in an alumina crucible. This crucible was then put in a Muffle with a temperature already set at 700°C and kept at this temperature for about 10 min. After that the crucible was taken out and cooled to the room temperature. The content of the crucible was then leached with hot water. The mixture was filtered through a Whatman GF-A membrane with a pore diameter of 0.4 μm. The filtrate was analyzed with ICP-AES to measure the concentration of chromium. The solid residue and the membrane were dried at 105°C for 4 h. Then the solid residue was removed from the membrane and weighed. The concentration of chromium in the filtrate was analyzed with ICP-AES.

The SEM sample was normally prepared by pouring a liquid composed of epoxy, thylene diamine and dibutyl phthalate on the sample powder placed at the bottom of a plastic mold. After standing for 12 h, a solidified sample was obtained. The sample was grinded and polished. The polished surface was sprayed with fine gold powder. Then the samples linked with double-sided carbon conductive tape on the surface was mounted on the SEM. The SEM observation was performed with the SEM (Zeiss Ultra 55). The X-ray diffraction (XRD) patterns of the fine sample powders with particle size less than 58–75 μm were recorded with a Rigaku TTRIII X-ray diffractometer equipped with a Cu Kα radiation source (λ=0.15405 nm). The diffraction patterns of XRD were analyzed using the software of X’Pert HighScore Plus. For the roasted pellet samples without hot water leaching, the samples were crushed and the particles thus obtained were used to make the SEM and XRD samples and alcohol instead of water was used in the SEM sample polishing. The sample particles required for XRD analysis were much fine than those for SEM analysis.

### 3. Results and Discussion

#### 3.1. Main Phases and CrOccurrence in the SSL Slag

The XRD patterns of the SSL slag was shown in Fig. 1. The main phases existed in the SSL slag were MgO, Ca3Mg(SiO4)2, Ca2SiO4, MgCr2O4 based on the XRD patterns (Fig. 1).

The SEM images of the original SSL was shown in Fig. 2. The chemical compositions and the possible phases of the slag particles postulated based on EDS analysis are presented in Table 2. Two types of phases were found in the slag particles. One type were the homogeneous phases shown in the regions of points 1, 2 and 3 (Figs. 2(a) and 2(b)), which were composed of Ca2SiO4, Ca2Mg(SiO4)2 and MgO (Table 2), respectively. The other was heterogeneous phases shown in the regions of points 4–8 (Figs. 2(c) and 2(d)), which were composed of Ca2SiO4 and Ca2Al2O3 etc. (Table 2).

The Cr-containing phases from the SSL slags were presented in Fig. 3. The Cr-containing spinel phase (Mg, Ca) (Cr, Fe)2O4 (Table 3) is found in the region indicated by point 1 of Fig. 3(a). The Cr+3 was present in the spinel phase in the form of MgCr2O4 (MgO-Cr2O3), which was insoluble in water. The Cr content in the spinel phase was 55 wt.% (Table 3). The spinel phase was embedded in silicate phase based on the EDS analysis. The spinel possessed higher melting point than those of the silicates. Therefore, when the liquid SSL slag cooled down during the stainless steel smelting, the solid spinel phases, which were the heterogeneous cores of precipitation, may be the nucleation sites of the liquid silicate.87 The Cr-containing silicate phases are shown in the regions indicated by point 3 of Fig. 3(b) and point 7 of Fig. 2(d). The Cr contents in the regions of points 3 and 7 were 1.0 wt.% (Table 3) and 0.6 wt.% (Table 2), respectively. The content of silicate was high in the SSL.

| Table 1. Chemical compositions of the original SSL slag and the leaching residue in wt.%.
|-----------------|-------|-------|-------|-------|-------|
| \(\text{Cr}_2\text{O}_3\) | CaO | MgO | SiO2 | Al2O3 | Na2O |
| SSL slag | 3.93 | 53.62 | 5.43 | 28.22 | 2.32 | 0 |
| residue | 0.10 | 49.95 | 6.17 | 19.65 | 4.13 | 6.97 |
| (*particle size of slag: 58–75 μm; †roasting conditions: 800°C, 3.5 h)
Based on the above results, it is postulated that most of chromium from the slag was contained in the spinel phase, which was embedded in the silicate phases. The Cr-containing metallic phase (Table 3) was found in the region indicated by point 2 of Fig. 3(a), which is mainly composed of Fe and Cr. The Cr content in the metallic phase was 9.5 wt.% (Table 3). During the stainless steel smelting, the metal droplets were enwrapped in liquid slag probably due to the oxygen agitation.

The Cr-containing spherical periclase (MgO) phase (Table 3) was found in the region indicated by point 4 of Fig. 3(c). The Cr contents in the surface and the internal core of the periclase phase (MgO) were 0.4 wt.% (Table 3) and 2.3 wt.% (Table 2), respectively. Because Mg content from the SSL slag is low (Table 1), it is inferred that the Cr content in the periclase (MgO) phase is also low.

In summary, most of chromium from the slag is contained in the spinel phase. In addition, the chromium is also found in the metallic phase and the periclase (MgO) phase. These three Cr-containing phases were embedded in silicate phases.

### 3.2. Phase Transformation during NaOH Roasting

The original SSL slag and the roasted pellets without hot water leaching were characterized by XRD and shown in Fig. 1. The main phases existed in the original SSL slag were Ca₃Mg(SiO₄)₂, Ca₂SiO₄, MgCr₂O₄ and MgO (Fig. 1). After the roasting for 3.5 h at 500°C, the main phases existed were Ca₃Mg(SiO₄)₂, Na₂CaSiO₄, CaO, MgO and Na₃CrO₄ (Fig. 1). The two phases of MgCr₂O₄ and Ca₂SiO₄ disappeared and three new phases of Na₃CrO₄, CaO, Na₂CaSiO₄ appeared at 500°C. It suggested that the following reactions might happen during the roasting at 500°C.

\[
\text{MgCr}_2\text{O}_4 + 6\text{NaOH} + \text{O}_2 \to 2\text{Na}_3\text{CrO}_4 + \text{MgO} + 3\text{H}_2\text{O} \quad \text{........................................(2)}
\]

\[
\text{Ca}_2\text{SiO}_4 + 2\text{NaOH} \to \text{Na}_2\text{CaSiO}_4 + \text{CaO} + \text{H}_2\text{O} \quad \text{........................................(3)}
\]

These two reactions may occur based on the thermodynamic calculations shown in the Fig. 4. Because available thermodynamic data of Na₃CrO₄ was not found, Na₃CrO₄
was replaced by Na₂CrO₄ during the thermodynamic calculations. The solubility of Na₃CrO₄ is unknown so far. The Na₃CrO₄ from the roasting products was probably converted to the very soluble Na₂CrO₄ during the hot water leaching, since the Cr extraction was 97% at 700°C for 2 h based on our experimental results, which will be reported elsewhere. In addition to the oxidation of MgCr₂O₄ indicated by point 1 of Fig. 3(a), the other low valence of chromium species such as Cr₂O₃ type indicated by the point 3 of Fig. 3(b), the point 4 of Fig. 3(c), the point 3 of Fig. 2(b) and the point 7 of Fig. 2(d) and the metallic Cr indicated by point 2 of Fig. 3(a) may also be oxidized to Na₂CrO₄. It will be discussed later. The involved oxidation reactions of the low valence of chromium species such as Cr and Cr₂O₃ are as follows.

4Cr + 3O₂ (g) = 2Cr₂O₃ .......................... (4)

Cr₂O₃ + 6NaOH + O₂ (g) = 2Na₃CrO₄ + 3H₂O .... (5)

After the roasting for 3.5 h at 600°C and 700°C, the main phases existed were Ca₃Mg(SiO₄)₂, Na₂CaSiO₄, CaO, Ca(OH)₂, MgO and Na₂CrO₄ (Fig. 1).

Compared to the case of 500°C, a new phase of Ca(OH)₂ appeared at 600°C and 700°C. It may happen according to the following reaction.

CaO + H₂O = Ca(OH)₂ ........................ (6)

This reaction may occur at the temperature range of 25°C to 1000°C based on the thermodynamic calculation (Fig. 4). After the roasting for 3.5 h at 800°C, the main phases existed were Na₂CaSiO₄, CaO, MgO and CaCrO₃ (Fig. 1). The three phases of Na₂CrO₄, Ca₃Mg(SiO₄)₂ and Ca(OH)₂ existed at 700°C disappeared and a new phase of CaCrO₃ appeared at 800°C. The possible reactions involved at the roasted slag during the water leaching according to the thermal calculation (Fig. 4).

For the roasting 3.5 h at 800°C, the main phases existing were Na₂CaSiO₄, CaO, MgO and CaCrO₃ (Fig. 1). The three phases of Na₂CrO₄, Ca₃Mg(SiO₄)₂ and Ca(OH)₂ existed at 700°C disappeared and a new phase of CaCrO₃ appeared at 800°C. The possible reactions involved at the roasted temperatures of 800°C, the main Cr-containing phase was CaCrO₃ and the valence state of chromium was +4 in this case. Both Na₂CrO₄ and CaCrO₃ were soluble during the water leaching, since about 96% of chromium could be extracted at both 700°C and 800°C under the optimal conditions according to our experimental results, which will be reported elsewhere. Maybe both Na₂CrO₄ and CaCrO₃ were converted to soluble Na₂CrO₄ during the hot water leaching. CaCrO₃ is an orthorhombic mineral.10) It has perovskite structure.10,11) It is very stable up to 1 200°C.10) Unfortunately, the solubility of CaCrO₃ is not reported so far. It is usually thought that Na₂CrO₄ is the product of chromite roasting with Na₂CO₃ addition. To our surprise, Na₂CrO₄ was not found in the roasting products of present work for all the temperatures studied. Instead, both Na₂CrO₄ and CaCrO₃ were found in the roasted pellets. This is a new discovery of this work, which is seldom reported before.

Since the three Cr-containing phases were embedded in the silicate phases as described previously, it is necessary to destroy the silicate phases to disclose the Cr-containing phases for the chromium extraction. It is noteworthy that the two main silicate phases of both Ca₃Mg(SiO₄)₂ and Ca₂SiO₄ in the original SSL slag took part in the reactions during the roasting. The phases of Ca₂SiO₄ and Ca₃Mg(SiO₄)₂ disappeared at 500°C and 800°C, respectively. It implied that the Ca₃Mg(SiO₄)₂ phase was more stable to resist the NaOH attack than the Ca₂SiO₄ phase.

3.3. Main Phases and Cr Occurrence in the Leaching Residues

Several same pellets with a weight of 3.52 g for each and a weight ratio of NaOH to slag of 0.6 was roasted at 800°C for 3.5 h. Then one roasted pellet was characterized with XRD and SEM. Another roasted pellet was leached with 100 mL of hot water of 90°C for 5 minutes. After that the mixture was filtered through a membrane. The solid residue and the membrane were dried at 105°C for 4 h. After that the solid leaching residue was removed from the membrane and collected for the characterization with XRD and SEM. In this way, the water leaching residue from one roasted pellet was obtained. The main phases for the roasted pellet without water leaching were Na₂CaSiO₄, CaO, MgO and CaCrO₃ (Fig. 5(a)). After water leaching, the main phases left in the leaching residue were CaCO₃, Na₂Ca₆(Si₂O₇)(SiO₄)₂ and MgO (Fig. 5(b)). It was inferred that CaO reacted with H₂O to form Ca(OH)₂ and then Ca(OH)₂ reacted with CO₂ from the air to form undissolved solid CaCO₃ during the leaching process. It was found that the contents of SiO₂ from the original slag and the leaching residue were 28.22 wt% and 18.65 wt%, respectively (Table 1). Thus, SiO₂ was lost from the roasted slag during the water leaching according to the following reaction.

6Na₂CaSiO₄ + 3H₂O =

Na₂Ca₆(Si₂O₇)(SiO₄)₂ + 6NaOH + 2Na₂SiO₃ .... (9)

It means that Na₂CaSiO₄ was soluble in water, which was also reported by Zhao et al.12) It is noteworthy that NaOH was also probably released from the Na₂CaSiO₄ to the water.

The SEM image of one area containing a fan-shaped par-
The leaching residue of roasted pellet was presented in Fig. 6(a). The Energy-dispersive X-ray spectroscopies (EDS) analyses of various elements in the area were presented in Figs. 6(b)–6(h). A smaller triangle particle was embedded in the bigger fan-shaped particle (Fig. 6(a)). Si, Ca and Mg were not present in the triangle particle (Figs. 6(c), 6(d), 6(h)). Na was dispersed everywhere inside the big fan-shaped particle including the small triangle particle (Fig. 6(b)). However, the quantity of Na in the triangle particle was less than that in the other places of the fan-shaped particle (Fig. 6(a)). Cr, Fe and O were present in the triangle particle (Figs. 6(e)–6(g)). It implied that the residual Cr was only present in a Fe–Cr–O phase, which was more resistant to NaOH attack. The residual chromium was not in the MgO phase. It implied that the chromium in MgO phase was also extracted at 800°C. The metallic phase of Fe–Cr alloy was not presented at 800°C based on the XRD pattern (Fig. 1).

3.4. The Possible Roles of NaOH in the Roasting Process

Under the same roasting conditions (800°C, weight ratio of NaOH or Na₂CO₃ to slag of 0.6, slag particle size of 48–58 μm), the Cr extraction with NaOH-added pellet was 96% at 120 minutes, while the Cr extraction with Na₂CO₃-added pellet was only 49% based on our experiments, which will be reported elsewhere. The oxidation of Cr³⁺ from MgCr₄O₇ to Cr⁶⁺ from Na₂CrO₄ at the temperature range of 0–1 000°C is more readily with NaOH-added pellet roasting than with Na₂CO₃-added pellet roasting based on the thermodynamic calculations (Fig. 4). This is the first reason to explain the discrepancy of Cr extraction between NaOH-added pellet roasting and Na₂CO₃-added pellet roasting.

The melting points of NaOH and Na₂CO₃ are 318°C and 851°C, respectively. The studied temperatures for NaOH-added roasting were generally between 500°C and 850°C, which were higher than 318°C. Thus the NaOH added to the SSL slag probably existed in liquid during the roasting. Compared to the solid Na₂CO₃ existing during the roasting, the flowing liquid NaOH may enter the deeper internal pores of slag particles and react with more chromium. This is the third reason to explain the discrepancy of Cr extraction between NaOH-added pellet roasting and Na₂CO₃-added pellet roasting.

The oxidation of chromium from the SSL slag with NaOH roasting was likely carried out in three phases (solid slag phase, liquid NaOH phase and air phase). The pellet before the roasting is shown in Fig. 7(a). The white points circled in Fig. 7(a) were the spherical particles of NaOH. After the roasting at 600°C for 0.5 h, the white particles on the pellet surface disappeared and some empty cavities were left in the original positions circled. It indicated that the NaOH particles had reacted with the slag phases such as the silicate phases. The possible reactions involved might be
represented by the reactions (2), (3) and (5).

After the NaOH-added roasting at 600°C for 0.5 h, many cavities appeared on the pellet surface (Fig. 7(b)). Many such cavities may also exist inside the pellet. Thus it is inferred that the appearance of these cavities facilitated the transfer of both O\(_2\) and liquid NaOH inside the pellet, which promoted the Cr oxidation and increased the Cr extraction.

3.5. Diffusion of Liquid NaOH Inside the Slag Particles

As described in paragraph 3.4, the oxidation of chromium from the SSL slag with the NaOH-added pellet roasting was likely carried out in three phases (solid slag, liquid NaOH, gaseous O\(_2\)). For the heterogeneous reaction, the reaction rate is normally controlled by mass transfer. The transfer rate \(v\) (m\(^2\)/s) of liquid NaOH in the porous slag is proportion to the driver gradient \(\nabla h\) (m).

\[
v = -C \frac{d^2 \rho g}{\mu} \nabla h \quad \text{.......................... (10)}
\]

Where \(C\) is a dimensionless constant associated with the pore geometry, \(d\) the pore diameter of the slag in m, \(\rho\) the density of the liquid NaOH in kg/m\(^3\), \(g\) the acceleration of gravity in m/s\(^2\), \(\mu\) the dynamic viscosity of the liquid NaOH in Pa\cdot s.

The transfer rate \(v\) of liquid NaOH is inversely proportion to its dynamic viscosity \(\mu\) based on the Eq. (10).

According to the literature data, \(^{14}\) the dynamic viscosity \(\mu\) of liquid NaOH has the following relationship with temperature \(T\) (K) at the temperature range of 350°C to 850°C.

\[
\ln \mu = - \frac{1066.1}{T} - 4.1216 \quad \text{.......................... (11)}
\]

It implies that the dynamic viscosity \(\mu\) of liquid NaOH is decreased while the transfer rate \(v\) of liquid NaOH is increased with increasing temperature, respectively, based on the Eqs. (10) and (11). The effect of the viscosity of liquid NaOH on the Cr extraction calculated by Eq. (1) was shown in Fig. 8. There was a dramatic decrease of NaOH viscosity with increasing temperature at the temperature range of 400 to 600°C, which accompanied a sharp increase of Cr extraction (Fig. 8). At the temperature range of 600 to 850°C, the NaOH viscosity decreased slowly with increasing temperature, which also accompanied a slow increase of Cr extraction (Fig. 8). It seems that the Cr extraction was inversely proportional to the viscosity of liquid NaOH.

In order to investigate the diffusion of liquid NaOH inside the sample particles during the roasting, the pellets roasted at various temperatures without water leaching were studied with SEM and presented in Fig. 9.

Fig. 7. The SEM morphologies of one NaOH-added pellet sample (a) prior to roasting and (b) after roasted at 600°C for 0.5 h with a weight ratio of NaOH to slag of 0.8 and a slag particle size fraction of 58–75 μm.

Fig. 8. Variation of the Cr extraction with temperature for 0.5 h with various weight ratios of NaOH to slag and a particle size fraction of 58–75 μm for the pellet samples. The variation of the viscosity of liquid NaOH with temperature.

In summary, both the bigger \(d_{\text{min}}\) (minimum particle pore diameter, which NaOH can enter) and the higher viscosity with liquid NaOH at 400°C are two main reasons to explain
In the absence of diffused O\textsubscript{2}, the oxidation of Cr\textsubscript{2}O\textsubscript{3} inside hindered the diffusion of external O\textsubscript{2} inside the particles closed the internal channels of the slag particles and thus structure began to collapse at 700 °C for the sample with a R value of 0.8. It is likely that the pellet decreased with the increasing temperature ranging from 600 to 850 °C. Therefore, it is inferred that a high Cr extraction was obtained only when liquid NaOH had diffused into the internal cores of the slag particles over 400 °C.

It is noteworthy that the Cr extractions at 500°C and 600°C were thus much higher than that at 400°C. Meanwhile, the liquid NaOH could diffuse into the internal cores of the slag particles only at the temperatures over 400°C. Therefore, it is inferred that a high Cr extraction was obtained only when liquid NaOH had diffused into the internal cores of the slag particles over 400°C.

It is noteworthy that the Cr extraction remarkably decreased with the increasing temperature ranging from 600 to 850°C for a R value of 0.8. It is likely that the pellet structure began to collapse at 700°C for the sample with a R value of 0.8. The collapsed structure probably reduced and closed the internal channels of the slag particles and thus hindered the diffusion of external O\textsubscript{2} inside the particles. In the absence of diffused O\textsubscript{2}, the oxidation of Cr\textsubscript{2}O\textsubscript{3} inside the particles to soluble sodium chromate became impossible based on the Eq. (5). This led to the a significant decrease of Cr extraction in the temperature range of 600–850°C for the sample with a R value of 0.8.

4. Conclusions

The thermochemical processes involved in the roasting of pellets composed of SSL slag and NaOH to extract chromium were studied. The mineral phases from the original SSL slag and the roasted pellets without or with water leaching were characterized by XRD and SEM. The following words conclude this study.

(1) It was found that Ca\textsubscript{3}Mg(SiO\textsubscript{4})\textsubscript{2}, Ca\textsubscript{2}SiO\textsubscript{4}, MgCr\textsubscript{2}O\textsubscript{4} and MgO are the main phases from the SSL slag. Most of chromium from the slag was present in spinel phase (MgCr2O4). In addition, the chromium was also found in metallic phase (Fe–Cr) and periclase phase (MgO). These three Cr-containing phases were embedded in the silicate phases.

(2) During the pellet roasting, the low valence of insoluble chromium species such as MgCr\textsubscript{2}O\textsubscript{4} were converted to Na\textsubscript{2}CrO\textsubscript{4} at the temperature range of 500–700°C and CaCr\textsubscript{2}O\textsubscript{4} at 800°C, respectively. The Na\textsubscript{2}CrO\textsubscript{4} and CaCr\textsubscript{2}O\textsubscript{4} were probably converted to Na\textsubscript{2}CrO\textsubscript{4} during the hot water leaching, since the both were soluble in hot water.

(3) After water leaching, the main phases left in the leaching residue were CaCO\textsubscript{3}, Na\textsubscript{2}Ca\textsubscript{6}(Si\textsubscript{2}O\textsubscript{7})(SiO\textsubscript{4})\textsubscript{2} and MgO and the residual chromium was only present in Cr–Fe–O phases. Part of NaOH was released from the roasted pellet into the hot water during the water leaching.

(4) It was found that the silicate phases of Ca\textsubscript{3}SiO\textsubscript{4} and Ca\textsubscript{3}Mg(SiO\textsubscript{4})\textsubscript{2} could be destroyed by NaOH at 500°C and 800°C, respectively.

(5) It was found that many cavities were left on the pellet surface after the roasting.

(6) It was found that a high chromium extraction was obtained only when the liquid NaOH had diffused into the internal cores of the slag particles over 400°C.

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