Analysis of Cr with Various Valence States in Industrial EAF Slag for Making Stainless Steel

Hui WANG,1) Baijun YAN2) and Fan LI3)*

1) Institute of Mineral Resource, Beijing General Research Institute of Mineral Metallurgy, Building 23, Zone 18 of ABP, No. 188, South 4th Ring Road West, Beijing, 100160 China. 2) Department of Physical Chemistry of Metallurgy, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, No. 30 Xue Yuan Road, Beijing, 100083 China. 3) Beijing Key Laboratory for Green Catalysis and Separation, Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, No.100 Ping Le Yuan Road, Beijing, 100124 China.

(Received on November 27, 2014; accepted on March 9, 2015)

Slags of stainless steel making by EAF process in one plant from south and the other from north China were selected. The qualitative and quantitative analysis of all elements in samples were investigated first, the possible phases were identified by diffraction. Micro-morphology and composition analysis showed that Cr exist in iron-based alloy, chromite phase and Cr-containing silicate phase. It inferred that Cr (0) would be in iron-based alloy drops, Cr (III) would be in chromite phase. The Cr valence states in slag were assumed as 0, +2, +3 and +6. The caustic plus carbonate sodium solution was adopted to leach Cr(VI) as CrO\(_4^{2-}\); oxalic acid was applied to leach the Cr(0) in alloy drops; FeCl\(_3\)-HCl-NH\(_4\)Cl combined with V\(_2\)O\(_5\)-HCl leaching process, the Cr(III) in slag would change to Cr\(^{2+}\) in solution; the resident containing Cr(III) was smelting by Na\(_2\)O\(_2\). Cr in different valence states were separated and detected. The optimized leaching processes of Cr (VI) and Cr (0) were investigated. The influence of the leaching process on existence of other phase was checked also. The analysis results showed the route of separation and analysis is suitable for the slag samples. Both slag samples were with the same trend of contents in various Cr states. Among the states, Cr (0) content is highest, about 2.0–4.5 mass%; the second highest content is Cr (III), about 1.4–2.7 mass%; the content of toxic Cr (VI) is about 80–310 ppm, the lest one is Cr (II), about 1.0–2.1 ppm. This study would provide an experimental method and basis for the utilization and environmental impact of stainless steel smelting slag.

KEY WORDS: analysis of Cr with various valence states; chemical quantitative analysis of different valence states; slag for making stainless steel; EAF slag.

1. Introduction

Chromium is an important alloy element in stainless steel. During refining process, part Cr is inevitably oxidized, and consequently Cr distributes between metal and slag. Because the different operating conditions during the refining process, such as oxygen partial pressure, temperature and so on, the chromium in slag may exist in different oxidation states normally the co-existence of divalent and trivalent chromium, sometime expressed as CrO and Cr\(_2\)O\(_3\), respectively. When industrial slag is cooled to ambient in air, it was reported that tiny amount of Cr in slag will be oxidized to hexavalent, and exists as CrO\(_4^{2-}\). In addition, some metal droplet is inevitably enwrapped in industrial slag. Therefore, the chromium in industrial slag exists in a series of oxidation states as 0 (elemental metal), +2, +3 and +6.

In steel industry, it is desired to measure the contents of different valent chromium in slag,\(^{1-6}\) because this information is related to the equilibrium and kinetic condition between metal and slag and could help to find the effective recycling process to making good use of the slag. In view of environmental protection, it is necessary to measure and separate the different valent chromium in slag. Because CrO\(_2^{2+}\) is dissolving in water, it may go into the water system arise the water pollution. Cr (VI) is poisonous for livings. Therefore, even it is tiny amount, this kind of slag containing Cr should be deposited and recycled in a specially designed method to prevent the impact to environment.\(^{7-9}\)

Scientists attempt to minimize the loss of Cr into slag and also need to treat this slag to meet the requirements of the environmental regulations if they are to be land-filled.\(^{10}\) To do these, the qualitative and quantitative analysis of Cr with different valence states in slag is the fundamental work. In the past, most works focus on the equilibrium systems in lab, there are only two valence states coexist. Because compositions of experimental slag were only oxides, analytical methods are relative simple. For the environmental investigations, only CrO\(_2^{2+}\), Cr (VI), was analyzed. There is no system investigation of Cr states in industrial EAF slag carried out until now.

* Corresponding author: E-mail: vanadiumli@bjut.edu.cn
DOI: http://dx.doi.org/10.2355/isijinternational.55.1425
Some researchers want to find the proper apparatus to investigate the amount of different valance states Cr in slag. Rietveld x-ray diffraction (XRD) quantitative analysis method might be a way to simulate and analyze the quantities of crystallized phases. But some amorphous phase in slag may cause large error. X-ray photoelectron spectroscopy (XPS),\textsuperscript{11–14} x-ray fluorescence (XRF),\textsuperscript{15} x-ray absorption near edge structure (XANES),\textsuperscript{11,14,16,17} high temperature mass spectrometric (MS) method combined with Knudsen effusion cell\textsuperscript{14,16} were reported to distinguish temperature mass spectrometric (MS) method combined absorption near edge structure (XANES).  

In the present work, slag sample of stainless steel making by EAF process in one plant from south and the other from north China were selected. Based on the qualitative and quantitative analysis of all elements in slag, phases indexed by XRD, micro-morphology observation by scanning electron microscopy (SEM) and composition analysis by energy dispersive spectroscopy of x-ray (EDS), the chemical route for separating and analyzing of different valence states Cr was designed. The optimized conditions were discussed also. Finally, the different Cr states in the two slag samples were determined.

### 2. Experimental

All the chemical reagents used in present work without any further purification. Main reagents except the standard samples are list in Table 1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular formula</th>
<th>Grade</th>
<th>Purity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium peroxide</td>
<td>Na₂O₂</td>
<td>A.R.</td>
<td>≥99 wt%</td>
<td>Sinopharm Company, China</td>
</tr>
<tr>
<td>sodium carbonate</td>
<td>Na₂CO₃</td>
<td>A.R.</td>
<td>≥99.8 wt%</td>
<td>Sinopharm Company, China</td>
</tr>
<tr>
<td>hydrochloric acid</td>
<td>HCl</td>
<td>A.R.</td>
<td>≥35 vol%</td>
<td>Sinopharm Company, China</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>C₂H₂O₄</td>
<td>A.R.</td>
<td>≥98 wt%</td>
<td>Sinopharm Company, China</td>
</tr>
<tr>
<td>phenylalanienurea</td>
<td>C₁₅H₁₄N₄O</td>
<td>A.R.</td>
<td>≥99.7 wt%</td>
<td>Sinopharm Company, China</td>
</tr>
<tr>
<td>sulfuric acid</td>
<td>H₂SO₄</td>
<td>A.R.</td>
<td>≥98 wt%</td>
<td>Sinopharm Company, China</td>
</tr>
<tr>
<td>sodium hydroxide</td>
<td>NaOH</td>
<td>A.R.</td>
<td>≥96 wt%</td>
<td>Sinopharm Company, China</td>
</tr>
<tr>
<td>Ammonium molybdate</td>
<td>(NH₄)₂MoO₂·4H₂O</td>
<td>A.R.</td>
<td>≥99.0 wt%</td>
<td>Sinopharm Company, China</td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td>FeCl₃·6H₂O</td>
<td>A.R.</td>
<td>≥98 wt%</td>
<td>Sinopharm Company, China</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>NH₄Cl</td>
<td>A.R.</td>
<td>≥99.8 wt%</td>
<td>Sinopharm Company, China</td>
</tr>
<tr>
<td>Zinc particle</td>
<td>Zn</td>
<td>A.R.</td>
<td>≥99.9 wt%</td>
<td>Xilong Company, China</td>
</tr>
<tr>
<td>Ammonium metavanadate</td>
<td>NH₄VO₃</td>
<td>A.R.</td>
<td>≥99.0 wt%</td>
<td>Yonghua Company, China</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>–</td>
<td>≥99.85</td>
<td>Prax gas company, China</td>
</tr>
<tr>
<td>Aluminium chloride</td>
<td>AlCl₃</td>
<td>A.R.</td>
<td>≥99.0 wt%</td>
<td>Alfa Aesar, USA</td>
</tr>
<tr>
<td>Sodium cyanide</td>
<td>NaCN</td>
<td>A.R.</td>
<td>≥98 wt%</td>
<td>Chengxin Company, China</td>
</tr>
</tbody>
</table>

A.R. represent Analytical reagent

### 2.1. Qualitative and Quantitative Analysis of All Elements

Samples were ground into powder passed through 200-mesh sieve (particle size was less than 74 micron (μm)). The sieved powder was weighed accurately (0.5000 g) and put into Ag crucible, and 10 times excessive amount of sodium peroxide plus sodium carbonate (mixing molar ratio 1:1) were added. The crucible with sample was heated to 750°C till the sample and reagents were melted completely. Then the crucible with sample was cooled down and put into a beaker, and 40 to 50 mL boiling water and some amount of hydrochloric acid were added till the sample was fully dissolved. The Ag crucible could be picked and washed by the deionized water, and the washed water was collected also with the solution. Through the above procedure, all the elements in slag sample were transferred into the solution. The solution cooling to ambient was moved to a certain volumetric flask and diluted to constant volume. Then, the metal elements in the diluted solution were qualitatively and quantitatively analyzed by induced coupling plasma-atomic emission spectroscopy (ICP-AES, Agilent™ 725ICP-OZS, USA). The sulfur in slag was measured by infrared radiation analyzer (LECO™ CS-344, USA). The silicon was analyzed by silica gravimetric method. The phosphorus was analyzed by a standard Molybdenum blue spectrophotometric method (REF: ISO 8556:1986 Title: Aluminum ores – Determination of phosphorus content – Molybdenum blue spectrophotometric method).

### 2.2. Phase Analysis

Morphologies of the slag samples were observed using a scanning electron microscope (SEM, Hitachi™ S-3500, Japan). The accelerate voltage is 40 kV, the filament current is 40 μA. The micro-composition analysis were carried out by the equipped energy dispersive spectroscopy of x-ray (EDS, Oxford™ INCA, GB). The crystalline phases in the
slag samples were characterized by X-ray powder diffraction (XRD) analysis (Rigaku\textsuperscript{TM} Ultima IV, Japan). The measurement is under Cu K\textalpha radiation operated at 40 kV and 40 mA; 2\theta scanning range is from 10 to 80\degree, 0.02\degree step; Scanning speed is 6\degree/min.

2.3. Chemical Analysis of the Different Oxidation States of Cr

The Cr(VI) in slag, in the form of CrO\textsubscript{4}\textsuperscript{2−}, was leached by sodium hydroxide and sodium carbonate to form the dissolvable NaCrO\textsubscript{4}\textsuperscript{2−}. Dissolved CrO\textsubscript{4}\textsuperscript{2−} was measured by a phenylanilieurea (another name is diphenylcarbazide) photometric method in acidic medium, by adding sulfuric acid.\textsuperscript{18} Ultraviolet-visible spectrophotometer (UV-vis, Purkinje\textsuperscript{TM} TU1810, China) is used, the wavelength is at 550 nm. To optimize the leaching conditions, the concentration of sodium hydroxide and sodium carbonate in solution were changed respectively. And the leaching temperature and time were investigated also. Caustic sodium may leach Si simultaneously, so Si content in leaching solution was investigated by molybdenum blue photometric method.\textsuperscript{18}

After Cr(VI) leaching, the solid residue was mixed with oxalic acid solution and then reflux at 100\degreeC for 2 hours, the Cr(0) would be oxidized to Cr(II) or Cr(III) and dissolved in solution.\textsuperscript{19} ICP-AES was applied to determine the content of Cr in solution, and the amount of Cr(0) in slag could be calculated. The effect of concentration of oxalic acid solution on the leaching of Cr(0) was studied.

About the separating and analyzing of Cr(II) and Cr(III) in slag, Wang and co-worker had reported a method.\textsuperscript{20} But it just a brief introduction, the detail procedure will be presented in this study. After removal of Cr(VI) and Cr(0) in slag, the solid residue was grind with FeCl\textsubscript{3}–HCl–NH\textsubscript{4}Cl system. AlCl\textsubscript{3} would help CaF\textsubscript{2} dissolving in the solution, so AlCl\textsubscript{3} was added to slag samples. This helps to overcome the bad impact of CaF\textsubscript{2} content during the sample leaching process. In the same time, the Fe\textsuperscript{3+} would help to change the CrO in slag to CrCl\textsubscript{3}. The mixture was moved to a sealed Erlenmeyer flask under the CO\textsubscript{2} protecting gas, and V\textsubscript{2+}–HCl solution was added. The added V\textsubscript{2+}–HCl solution would reduce the CrCl\textsubscript{3} to Cr\textsuperscript{2+} again. V\textsubscript{2+}–HCl solution was produced by vanadate mixed with hydrochloric acid solution and react with zinc particles. The ICP-AES method was applied to detect the Cr\textsuperscript{2+} amount in leaching solution. The content of Cr(II) in slag could be calculated. The solid residue in Erlenmeyer flask only containing Cr(III). It was collected and mixed with sodium peroxide. During molten process the Cr(III) would be oxide to Cr(VI), CrO\textsubscript{2}\textsuperscript{2−}, and dissolved in water. Then the solution was diluted to the proper range of concentration, phenylanilieurea photometric method was applied to determine the concentration of CrO\textsubscript{4}\textsuperscript{2−}; the amount of Cr(III) in slag could be calculated.

3. Results and Discussion

3.1. Analysis of Elements in Slag

The slag samples of stainless steel making by EAF process in one plant from south China (sample 1) and from north China (sample 2) were treated as the method describe in section 2.1. Based on the qualitative and semi-quantitative analysis, Li, Na, K, Ca, Si, Mg, Al, Mn, V, Ti, Fe, Cr, S and P were the component elements. Results were listed in Table 2. Compared these two results, except S, Cr and Fe, the contents of other elements are in the same scale, and the values are only slightly different. The contents of Cr and Fe in sample 1 is about two times of that in sample 2, whereas the content of S in sample 1 is about one sixth of that in sample 2. Obviously, the sample 2 has high desulfurizing ability and low loss of Cr and Fe, i.e., the sulfide capacity of slag 2 is higher that of slag 1. Therefore, to clarify the distribution of different oxidation states Cr in these two slags are necessary and meaningful.

3.2. Micro-morphology, Composition Analysis and Diffraction

Figures 1 and 2 are the delegated SEM morphologies with the EDS micro composition analysis from sample 1 and 2 respectively. Both in Figs. 1 and 2, there are light white, light grey and dark grey 3 different phases. The EDS result shows that the main elements in the light white phase are Fe and Cr without O, it should be the metal drop enwrapped in the slag; In the light grey phase, there are majority of Cr with large amount of O, Mn, Mg, Al, Fe and Ca in minor amount, it would be the complex oxide containing large amount of Chromium; In the dark grey phase, it contains large amount of Ca, Si and O, like the calcium silicate but contain some Mg, Al, Mn, Ti, Cr, Fe elements.

The XRD patterns of sample 1 and 2 are shown in Fig. 3. It can be seen that the phases in these two samples identified by XRD are slightly different. The chromferide and chromite phases existed in the both sample, but the calcium silicate phase only appeared in sample 2. It can be concluded that chromferide phase is the light white phase observed in the SEM microphotograph, and the diffraction peaks of chromite phase should attribute to light grey phase in the SEM microphotograph. It is well known that the quickly cooled silicate melt possess structure like glass and it can not generate sharp peaks in XRD pattern. If the silicate melt was cooled slowly, crystal phase will crystalized. So, it can be thought that the dark grey phase observed in SEM measurement should be complex silicate, and it possessed glass like structure in the sample 1, but crystalized to a certain extent in the sample 2.

In the chromferide phase, the valance state of Cr is 0. The chromium in the chromite phase is +3. There is no Cr(II) and Cr(VI) found in the diffraction results. This imply that either the Cr(II) and Cr(VI) exist in the complex silicate phase or the amount of Cr(II) and Cr(VI) are too low to detect.

<table>
<thead>
<tr>
<th>Table 2.</th>
<th>Comparison results of analysis from two slag samples.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Sample 1, wt%</td>
</tr>
<tr>
<td>Mg</td>
<td>1.70</td>
</tr>
<tr>
<td>Na</td>
<td>0.53</td>
</tr>
<tr>
<td>K</td>
<td>0.56</td>
</tr>
<tr>
<td>Ca</td>
<td>19.83</td>
</tr>
<tr>
<td>Li</td>
<td>0.026</td>
</tr>
<tr>
<td>P</td>
<td>0.010</td>
</tr>
<tr>
<td>S</td>
<td>0.037</td>
</tr>
</tbody>
</table>
detect by XRD and SEM.

From above analysis, we speculate the chromferide phase (metal drop) contain the Cr(0), Cr(III) exist in the chromite phase, and calcium silicate might embrace the Cr(II) inside but adsorbed and isolated CrO$_4^{2-}$, Cr(VI) on its surface. Based on the results and hypothesis above, the separation and analytical method of Cr in different valence states was designed.

3.3. Chemical Phase Analysis

It is assumed that Cr(0), Cr(II), Cr(III) and Cr(VI) are co-existence in the slag. Based on the results of elements analysis, diffraction, micro-morphology and composition analysis, a possible route of chemical analysis of Cr element...
with different valence states was designed (Fig. 4).

The Cr(VI) is the highest states among Cr, it was formed during the cooling process of slag. Therefore, it would be exposed on the surface of the slag samples. The Cr(VI) was leached by the solution combined the caustic and carbonate firstly. The solution containing Cr(VI) was separated from the leaching system as soon as possible, otherwise it would impact the Cr(0) and Cr(II) leaching process by redox reaction via thermodynamic consideration. Among the complex oxides in slag, caustic sodium might be aggressive to silicate (complex silica). If the silicate in slag is dissolved, the low state Cr inside the silicate would be seriously oxidized by high state Cr.

The Cr(0), in the metallic state, exists in the metal drop in slag. The leaching process of Cr(0) should avoid to impact the oxides containing Cr(II) and Cr(III). Therefore, weak acid, oxalic acid was selected. It could change the Cr(0) to Cr$^{2+}$ first, and because the $\varphi_{Cr^{0}/Cr^{2+}} = -0.86 \text{ V}$, $\varphi_{Cr^{2+}/Cr^{3+}} = -0.41 \text{ V}$, some Cr$^{2+}$ may oxide to Cr$^{3+}$, and Cr$^{3+}$ could let Cr(0) change to Cr$^{2+}$ also. The final result is Cr(0) in metal droplet change to Cr$^{2+}$ or Cr$^{3+}$ in solution. The Cr(III) in sample is not attack by the oxalic acid. Cr (II) in sample may dissolve in this leaching process. As narrated in section 3.2, Cr (II) may embrace in calcium silicate; the oxalic acid could not attack silicate to leaching the Cr (II). So it was believed that very few amount of Cr (II) exposed on the surface of silicate affected by this leaching process. This only can bring tiny system error.

Based on our provirus study, the Cr(II) in slag would transfer to CrCl$_3$ in the FeCl$_3$–HCl–NH$_4$Cl solution. The V$^{2+}$ in hydrochloric acid solution would reduce the CrCl$_3$ to Cr$^{2+}$. The amount of Cr$^{2+}$ in solution represent the Cr(II) in slag. After removal the Cr(VI), Cr(0) and Cr(II), the rest Cr in slag is Cr(III). It could be oxidized to CrO$_4^{2-}$, the Cr(VI), to measure the concentration.

### 3.3.1. Optimization of the Conditions for Leaching Cr (VI)

Conditions for leaching Cr(VI) include the concentrations of caustic and carbonate, leaching time and operation temperature. Serial experiments were designed to find the optimized running condition.

The concentration of sodium carbonate were fixed at 0.3 wt%, leaching time was fixed at 480 min, the operation temperature was 373 K, only the concentration of caustic (sodium hydroxide) changed from 0.15 to 5.00 wt%. The detected concentration of Cr(VI) were listed in Table 3. From Table 3, it could find that if the concentration of caustic is lower than 0.19 wt%, the detected amounts are lower than others. It inferred that the amount of caustic is not enough to leach all the Cr(VI) in the sample. The concentration of caustic should larger than 0.19 wt%.

Leaching time is another factor that impacts the recovery efficient. The concentrations of caustic and carbonate are fixed at 0.19 wt% and 0.3 wt% respectively, the temperature was fixed at 373 K, the effect of the leaching time on the detected concentration of Cr(VI) was investigated. The results were listed in Table 4. When leaching time is shorter than 55 min, there was still some Cr(VI) remain in slag. When the leaching time set 55 min or even longer.

Temperature is another factor that impacts the recovery efficient. The concentrations of caustic and carbonate are fixed at 0.19 wt% and 0.3 wt% respectively, the temperature was fixed at 373 K, it affects the effect of the leaching time on the detected concentration of Cr(VI) was investigated. The results were listed in Table 4. When leaching time is shorter than 55 min, there was still some Cr(VI) remain in slag. So the leaching time should set 55 min or even longer.

Temperature is an important thermodynamic and kinetic factor to leaching reaction. All the other conditions, except the temperature, are fixed as the investigation of reaction time, the reaction time is 55 min, and the influence of temperature was studied. Results were plot in Fig. 5. It showed
The effect of concentrate (0.15%–5.00 wt%) of caustic may react with Cr (VI) and arouse the big error in analysis. The caustic and carbonate leaching solution, but the silicates containing in metal drop, chromic transition metal salts and silicate slag phases. The first two phases may not affect by leaching time is no less than 55 min.

According to the XRD and SEM-EDS analysis, Cr is contained in metal drop, chromic transition metal salts and silicate slag phases. The first two phases may not affect by the caustic and carbonate leaching solution, but the silicates may dissolve in the solution. The lower Cr valence state of concentrate (0.15%–5.00 wt%) of caustic

that the amount of leaching Cr (VI) were in the same level from 363 to 373 K. But when the temperature dropped to 358 K, the amount of leaching Cr (VI) dropped also. The leaching temperature should be no less than 363 K. Sum up, in order to obtain the stable analysis result, the leaching condition is selected that the concentrations of caustic and carbonate are fixed at 0.19 wt% and 0.3 wt% respectively, the temperature was fixed at 373 K, and the leaching time was no less than 55 min.

According to the XRD and SEM-EDS analysis, Cr is containing in metal drop, chromic transition metal salts and silicate slag phases. The first two phases may not affect by the caustic and carbonate leaching solution, but the silicates may dissolve in the solution. The lower Cr valence state of concentrate (0.15%–5.00 wt%) of caustic

on the leaching of Cr (VI) was investigated, at the same time the dissolving of Si was detected also. It is found that the maximum Si content is 0.005 ppm. the silicates were believed safely in this leaching system, this leaching process may few affect other states of Cr in samples. In such alkali system, the solubility of Fe$^{2+}$ and Fe$^{3+}$ was very few; we believed that when Cr (VI) was leaching rare iron species was dissolving.

3.3.2. Optimization of the Conditions for Leaching Cr (0)

After extracted Cr (VI), slag samples were adding oxalic acid in different concentration and refluxing at higher than 373 K for 120 min. then filtered the mixture, the amount of Cr$^{2+}$ in solution was detected by ICP-AES. Results from different concentration of oxalic acid were listed in Table 5. The concentration of oxalic acid is optimized at 7–8 wt%. 7 wt% oxalic acid solution was selected in present work.

3.3.3. Separation and Analysis of Cr (II)

When the Cr(VI) and Cr(0) were removed from the slag, there were Cr(II) and Cr(III) in slag samples. The chemical phase analysis of slag containing Cr(II) and Cr(III) by FeCl$_3$–HCl–NH$_4$Cl leaching process and V$^{2+}$–HCl phase transformation method was reported in our previous work. Here is the brief introduction. Fe$^{3+}$ in solution could help to dissolve the CrO, Cr(II), in slag. The reaction is

\[ \text{Fe}^{3+} + 3\text{Cl}^- + \text{Cr}^0 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{CrCl}_3 + \text{H}_2\text{O}, \ldots (1) \]

CrO transfer to CrCl$_3$, and the V$^{2+}$ would reduce it to Cr$^{2+}$ in solution. This process could avoid some amount of Cr$^{3+}$ with large amount of Cl$^-$ to form CrCl$_3$·6H$_2$O solid. Cr$^{2+}$ is with larger solubility than that of Cr$^{3+}$ in this solution. The reduction reaction is

\[ 3\text{CrCl}_3 + \text{V}^{2+} + 4\text{H}_2\text{O} \rightarrow \text{V(OH)}_2^+ + 3\text{Cr}^{2+} + 4\text{H}^+ + 9\text{Cl}^- \]

The dissolving Cr$^{2+}$ should avoid oxidize in the Erlenmeyer flask which filled with CO$_2$ gas. Reactant V$^{2+}$ was obtained from the reaction of metavanadate and metal zinc. It describes as below:

\[ 2\text{VO}_3^- + 3\text{Zn} + 12\text{H}^+ \rightarrow 2\text{V}^{2+} + 3\text{Zn}^{2+} + 6\text{H}_2\text{O}, \ldots (3) \]

The Cr$^{2+}$ obtained from reaction (2) was directly reflect the amount of CrO, Cr(II), in slag. ICP-AES method was adopted to measure the Cr$^{2+}$ in solution. Some slag may contain CaF$_2$, the AlCl$_3$ in solution could help to dissolve the CaF$_2$, some AlCl$_3$ was added during the sample dissolving process. The final result showed that there are 2.10 ppm and 1.05 ppm Cr (II) containing in Sample 1 and sample 2 respectively.

3.3.4. Analysis of Cr (III)

After the operation 3.3.1 to 3.3.3, the only state of Cr in rest slag is Cr(III). Mixing these slag with sodium peroxide and heat the mixture to the molten temperature, Cr(III) would oxide to Cr(VI), CrO$_2$$^{2-}$, which is dissolving in aqueous solution. The amount of CrO$_2$$^{2-}$ could determined by phenylalanilueare photometric method at the 550 nm wave-length theoretically. But during the operation, it is found that the result is not stable and reproducible, the redox couple of

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Fe\(^{2+}/\text{Fe}^{3+}\) from the dissolving of the slag would affect the chemical state of Cr in solution. To overcome this problem, sodium cyanide was introduced before the 3.3.3 Separation chemical state of Cr in solution. To overcome this problem, Fe\(^2+\) with Fe\(^3+\) would co-ordinate with Fe\(^{2+}\) ligand to form the complex compound. After this modification the measured data of Cr(III) in slag are stable and reproducible. There are 2.65 wt% and 1.45 wt% Cr (III) containing in Sample 1 and sample 2 respectively.

4. Summary

Two slag samples of stainless steel making by EAF process, one from a plant in south China the other from a plant in north China, were selected. Based on the analysis of elements, XRD phase analysis and SEM-EDS micro-analysis, the route of chemical phase analysis was designed. After serials of experiments, at 363 K, 0.20 wt% caustic and 0.3 wt% carbonate aqueous solution was applied to leaching Cr(VI). The whole process was at least 55 min long. The 7–8 wt% of oxalic acid solution was reflux under boiling for 120 min for the Cr(0) extraction. The rest slag sample mixed with NaCN solution and applied the method from reference 20 to determined the Cr(II) and Cr(III) in slag. The contents of different Cr states of two samples were listed in Table 6. The derivation of the sum of different contents of states and the total Cr in measurement is less than <1.55%. The results are reliable.

Acknowledgement

The financial supports on the project 51104020, 51172007, 51174021, 50974011 and 51472009 from National Natural Science Foundation of China, the project 2120001 from Beijing Natural Science Foundation and the project FRFT-09-003A from the Fundamental Research Funds for the Central Universities are gratefully acknowledged.

**REFERENCES**