



# **Advances towards a Clean Hydrometallurgical Process for Chromite**

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**Abstract:** Because of the acute toxicity of Cr(VI)-bearing substances, the pollution problem caused by chromite process residue has become a worldwide concern. In the view of relevant studies, the technologies based on the alkali treatment cannot fundamentally resolve the pollution problem, because the oxidation of Cr(III) to Cr(VI) is unavoidable during chromite decomposition. In contrast, the oxidation of Cr(III) to Cr(VI) can be controlled by the sulfuric acid treatment of chromite, and the Cr(VI) pollution can be eliminated from the original source of production. Many research studies focusing on the resolutions of the key obstacles hindering the development of the sulfuric acid treatment process have been carried out, and significant progress has been achieved. In this study, a clean hydrometallurgical process without the generation of hexavalent chromium is demonstrated. First, the chromite was decomposed and leached by sulfuric acid solution in the presence of an oxidant. Then, iron was hydrothermally removed from the acid solution as the precipitate of jarosite. Finally, chromium salts were obtained by adjusting the basicity of the solution, separation and drying. With the aim of realizing industrialization, future research emphasis on the development of the sulfuric acid treatment process is proposed in this study.

**Keywords:** chromite; chromium salt; Cr(VI) pollution; sulfuric acid leaching; separation of  $Cr^{3+}$  and  $Fe^{3+}$ 

## 1. Introduction

Chromium salts play an important role in the national economy and are widely used in metallurgy, chemical industry, military, textile, and machinery. Among the chromium salts, the consumption of basic chromium sulfate and chromium oxides accounts for more than half of the total consumption, in addition to chromium acetate, chromium chloride, and chromium salts of organic acids. In recent years, the chromium salt industry in China has made significant progress in terms of production scale, equipment level, product quality, and environmental protection awareness. Since 2000, the chromium salt production capacity of China has surpassed the U.S., ranked the first in the world, with an average annual growth rate of 10%. In 2005, China's total production of chromium salt reached 259 thousand tons [1], which further increased to 363 thousand tons by 2011, accounting for 37.3% of the world's chromium salt production [2]. With the rapid development of the chromium salt industry, the pollution problem caused by the decomposition of chromite, the main raw material for chromium salt preparation, has become more and more serious. The residual chromium-containing materials after the extraction are either left on site or used as landfill. Some chromate compounds found in the leftover residues are highly soluble and migrate via the surface and ground water, threatening human health and the environment. The highly soluble chromates pass through concrete walls in many buildings and threaten the occupants, resulting in the evacuation and closure of buildings [3]. In China, the annual emission of 300,000 tons of highly toxic chromium residue and large amounts

of chromium-containing dust has seriously worsened the surrounding environment [4]. A shocking incident was reported previously, where 1800 water wells were scrapped because of the chromium residue pollution in Northeast China. In addition, chromium salt factories in Shanghai, Qingdao, Yixing, and other domestic cities were forced to shut down because of the pollution problem [5].

At present, the pollution caused by the chromium salt industry has become a worldwide environmental issue that has repeatedly arisen in the U.S., Japan, and other developed countries. For example, the American AlliedSignal Company was forced to shut down and the chromium salt factory in Germany had to be moved from Bayer to South Africa because of serious pollution [6,7]. Therefore, the development of a clean treatment process for chromite has become a significant concern.

## 2. Chromium Salt Preparation Technology

Chromium-bearing ores are found in many forms, but the economically extractable form is mineral chromite, which is inert and insoluble in water in its spinel form. Chromium exists in various oxidation states, but the common and stable chemical states are trivalent and hexavalent chromium [8]. For chromium salt preparation, the water-insoluble Cr(III) (chromite) is converted into the water-soluble Cr(VI) in alkaline solution in the presence of an oxidant, followed by the separation of the insoluble gangue from the leachate containing Cr(VI) by physical separation. As a result, the majority of chromium salt preparation technologies are based on the alkali oxidizing treatment of chromite because of the low oxidation potential of Cr(III) to Cr(VI) in alkaline environment, following the reactions shown in Equations (1)–(3) [9]. The soluble chromate compounds leach during the extraction process, and Cr(III) salts can be prepared by the reduction of sodium dichromate (Na<sub>2</sub>CrO<sub>4</sub>) [10–12]. However, the residual chromate slowly dissolves and is left behind in the ore residue, comprising chemical compounds such as calcium chromate (CaCrO<sub>4</sub>) with a solubility of 0.00071 mol·kg<sup>-1</sup> in water at 20–30  $^{\circ}$ C and iron oxide [13,14]. As the acute oral lethal dose of Cr(VI) compound is 115 g, and the water containing >0.1 mg  $L^{-1}$  of Cr(VI) is poisonous to the human body [15], the U.S. Environmental Protection Agency (EPA) classifies Cr(VI) as a Group A Human Carcinogen [8]. Hence, the alkali oxidizing treatment of chromite seriously threatens the environment and human health.

$$FeCr_2O_4 + 2Na_2CO_3 + 7/4O_2 = 2Na_2CrO_4 + 1/2Fe_2O_3 + 2CO_2$$
(1)

$$Fe_2O_3 + Na_2CO_3 = 2NaFeO_2 + CO_2 \uparrow$$
(2)

$$FeCr_2O_4 + 4NaFeO_2 + 7/4O_2 = 2Na_2CrO_4 + 5/2Fe_2O_3$$
(3)

The calcium-roasting treatment process, a typical alkaline process, of chromite is widely used in China [16]. The silicon, aluminum, and iron in chromite react with calcium oxide to form insoluble calcium silicate and calcium alumino-ferrite; therefore, the impurity in the Cr(VI)-rich leachate could be reduced [17]. In this process, a large amount of highly toxic emissions including Cr(VI)-bearing residue, gas, and dust is generated, posing a serious threat to the environment. Moreover, the discharge of toxic residue containing Cr(VI) is linked to a low recovery of chromium, usually in the range of 75%–81%. According to surveys, the toxic residue of industrial chromium salts is mainly linked to sodium dichromate production. The preparation of one ton of sodium dichromate can generate  $\sim$ 2.5 tons of residue, in which the Cr(VI) content is  $\geq$ 0.4%, present in the carcinogenic calcium chromate phase [18,19].

The non-calcium roasting process has been gradually adapted to replace the calcium-roasting process in the developed chemical industries such as at the Occidental Chemical Company in the U.S. and the Elementis Chemical Company in the UK [20]. In this process, the calcium reagent is replaced by reactive recycling residue, thereby sharply decreasing the discharge of toxic residue, especially carcinogenic calcium chromate [21]. The recycling residue with a particle size of  $\geq$ 75 µm is recovered from the leached residue after air oxidation, wet milling, and leaching in the non-calcium roasting process, comprising chromite, MgO, NaAlSiO<sub>4</sub>, Na<sub>4</sub>MgAl<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>, 6NaAlSiO<sub>4</sub>· Na<sub>2</sub>CrO<sub>4</sub>,

 $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Mg(Fe,Al)<sub>2</sub>O<sub>4</sub>, and others [22,23]. According to the various technical procedures, the non-calcium roasting process can be divided into different technologies such as no-padding granulation technology [24,25], wet pelletizing technology [26], tri-roasting and bi-leaching technology [27], bi-roasting and neutral leaching technology [28], preheating single-roasting technology [29], oxidizing roasting technology with carbon ferrochrome [30], and pre-roasting technology by controlling silicon and aluminum [31]. Wang *et al.* [4] found that in the non-calcium roasting process, the recovery of chromium could reach >90%. In this process, the amount of chromic residue can be reduced to one-third of that in the calcium-roasting process, and the Cr(VI) content in the residue drops to one-tenth. In addition, almost no carcinogenic calcium chromate is found in the residue from the non-calcium roasting process are roughly the same as the calcium-roasting process, hence Cr(VI) compounds are still generated [32,33]. In summary, the non-calcium roasting process cannot completely solve the problem of Cr(VI) pollution, even though the amount of toxic residue is significantly reduced [34].

The liquid phase oxidation technology for chromite in molten (or sub-molten) salt was proposed by the Institute of Process Engineering, at the Chinese Academy of Sciences, and later became a burgeoning treatment process for chromium salt preparation [10,35]. In this process, the chromite suspended in the molten (or sub-molten) alkaline medium is decomposed by oxidation, and then the chromium salt is prepared by separation, filtration, and purification steps. In relation to the liquid phase oxidation process of chromite in molten (or sub-molten) salt, a significant number of thermodynamic and kinetic studies have been conducted, indicating that this process possesses a strong reaction tendency [36–40]. Zhang *et al.*, in collaboration with the Zhenxin chemical company in the Henan province of China, built a demonstration pilot-scale process with an annual output of 8000 tons of potassium chromate to produce high-quality chromium salts [5]. The reaction temperature and energy consumption were both effectively decreased compared to those in the traditional technologies.

Xu *et al.* [41] decomposed chromite in NaOH solution in the presence of oxidizing gases including  $O_2$ , air,  $O_3$  or their mixtures, and then prepared sodium chromate by pressure leaching. In this process, sodium dichromate and chromium anhydride are produced from sodium chromate by the electrolytic method. Wang *et al.* [42] utilized an electrochemical field to enhance the oxidative decomposition of chromite in a KOH sub-molten salt medium, affording the maximum extraction of chromium as 99%. In the aforementioned processes, the consumption of electricity is high, even though the discharge of toxic residue is limited. Hemmings *et al.* adapted a hydrothermal process with vacuum evaporation to treat chromite and successfully prepared chromic anhydride and sodium bisulfate [2]. Notably, none of the above-mentioned processes has achieved commercial-scale production.

As stated above, although many studies have been carried out to improve the chromium salt production process, none of these breaks away from the basic principle of oxidizing Cr(III) to Cr(VI) for chromite decomposition. As a result, the pollution problem caused by Cr(VI)-bearing substances in the chromium salt industry has not yet been resolved. Cr(III) is insoluble in alkaline solution; however, it is soluble in sulfuric acid solution. The oxidation from Cr(III) to Cr(VI) is therefore avoided in the sulfuric acid treatment process, which is cleaner and more environmentally friendly compared to the alkaline treatment process. Nevertheless, two obstacles hinder the development of the sulfuric acid treatment process: (i) the chromium in the chromite is difficult to leach because of the high stability of the chromite spinel in sulfuric acid solution at room temperature and atmospheric pressure; (ii) iron, magnesium, and aluminum ions can be released into the leachate concomitantly as chromium is leached, and the removal of impurities is especially difficult for the separation of Fe<sup>3+</sup> and Cr<sup>3+</sup>. With increasing requirements for environmental protection, the development of a sulfuric acid treatment process has attracted significant attention, and the resolution of the two obstacles has become a worldwide focus of research.

#### 3. Leaching Process of Chromite in Sulfuric Acid Solution

The term "chromite" refers to chromium-containing spinels, with a composition of  $AO \cdot B_2O_3$ , where the divalent cation A can be  $Fe^{2+}$  or  $Mg^{2+}$ , and the trivalent cation B can be  $Fe^{3+}$ ,  $Cr^{3+}$ , or  $AI^{3+}$  [43]. Chromite spinel (FeCr<sub>2</sub>O<sub>4</sub>) is the main mineral phase of the chromite ore [44]. As shown in Figure 1, chromite spinel belongs to the cubic system, in which the 32 oxygen atoms stack in the central plane of the large cubic cell, forming 64 tetrahedral voids and 32 octahedral voids [45]. For the classic chromite spinel, among these voids, eight tetrahedral sites are occupied by Fe(II) and 16 octahedral sites are occupied by Cr(III). Chromite spinel has a stable and compact spinel lattice structure that is barely soluble in sulfuric acid solution at room temperature and atmospheric pressure. For the chromite ore in nature, a part of the Fe(II) can be replaced by Mg(II) and a part of the Cr(III) can be replaced by Al(III) or Fe(III). Thus, (Mg,Fe)(Cr,Al,Fe)<sub>2</sub>O<sub>4</sub> as the chromium-bearing phase is isomorphic, in which Mg(II) and Fe(II) occupy the tetrahedral sites of the lattice, whereas Cr(III), Al(III), and Fe(III) occupy the octahedral sites of the lattice, whereas Cr(III), Al(III), and Fe(III) occupy the octahedral sites of the lattice, whereas Cr(III), Al(III), and Fe(III) occupy the octahedral sites of the lattice, whereas Cr(III), Al(III), and Fe(III) occups the octahedral sites of the lattice, whereas Cr(III), Al(III), and Fe(III) occups the octahedral sites of the lattice, whereas Cr(III), Al(III), and Fe(III) occups the octahedral sites of the lattice, whereas Cr(III), Al(III), and Fe(III) occups the octahedral sites of the lattice, whereas Cr(III), Al(III), and Fe(III) occups the octahedral sites of the lattice, whereas Cr(III), Al(III), and Fe(III) occups the octahedral sites of the lattice, whereas Cr(III), Al(III), and Fe(III) occups the octahedral sites of the lattice, whereas Cr(III), Al(III), and Fe(III) occups the octahedral sites of the lattice site occups the octahedr



Figure 1. Crystalline structure of chromite spinel [45].

With the aim to investigate the leaching thermodynamics of chromite in sulfuric acid solution, a potential (E)-pH diagram for the Fe-Cr-H<sub>2</sub>O system based on the principle of simultaneous equilibrium was developed using Factsage 6.4, as shown in Figure 2 [48]. In all the colored regions, chromium is soluble as either  $Cr^{3+}$  or  $Cr_2O_7^{2-}$ . However, to realize the dissolution of Cr(III) from chromite, only the potential and pH values in the green and the blue regions should be chosen based on the following reasons. In the red region, the chromium in  $Cr_2O_7^{2-}$  is Cr(VI), which is toxic. In the yellow region, although the chromium in  $Cr^{3+}$  is Cr(III), the valence of iron is same as that in the chromite spinel, and the structure of the spinel is difficult to disrupt, because no oxidation reaction occurs. Hence, only in the green and blue regions can chromium in the chromite spinel be dissolved effectively in the form of  $Cr^{3+}$  by the oxidation of Fe(II) to Fe(III). Clearly, an appropriate oxidation potential and low pH value are essential for the decomposition of chromite spinel and, in particular, the oxidation potential plays a key role in preventing the generation of Cr(VI).

Biermann *et al.* [49] investigated the decomposition mechanism of chromite by sulfuric acid. The initial step involves the attack of protons on the chromite lattice, bringing the metallic constituents into the solution in a similar ratio as that in the lattice. The second step is the precipitation of polynuclear products that can slow down the attack on the chromite. The extraction of chromium by leaching in sulfuric acid is limited without an oxidant. With the goal of improving the leaching behavior of chromite in sulfuric acid solution, Geveci *et al.* [50] used perchloric acid as the catalyst in the leaching process at atmospheric pressure, achieving 83% chromium extraction. Vardar *et al.* [51] determined that the apparent activation energy for the leaching of chromite in sulfuric acid at atmospheric pressure is 77 kJ· mol<sup>-1</sup> in the presence of perchlorate. Shi *et al.* [52,53] used sodium bichromate as an oxidant in the leaching process at atmospheric pressure and 110–170 °C, achieving a chromium extraction of 82%. All of the above investigations indicate that no Cr(VI) was generated in the sulfuric acid leaching

process. It is still worth noting that the extraction of chromium is not sufficiently high, probably because of the inappropriate choice of oxidant. Liu *et al.* [54–56] found that adding a certain amount of oxidant could notably improve the chemical potential of the sulfuric acid solution, thus significantly accelerating the chromite sulfuric acid leaching process, e.g., the extraction of chromium was 93% without the generation of Cr(VI).



Figure 2. E-pH diagram of the Cr-Fe-H<sub>2</sub>O system.

Zhao *et al.* [57,58] investigated the sulfuric acid leaching behavior of chromite in the presence of oxidant affording the optimal chromium extraction of 96.4%. The sulfuric acid leaching behavior of the chromite in Zhao *et al.*'s study can be illustrated as shown in Figure 3, where four types of spinel, denoted as I, II, III, and IV, represent different states at specific stages of the leaching process. Spinel I shows that the particle becomes smaller with the duration of the leaching. Three corrosion depths marked as  $D_{b(p)}$ ,  $D_{b(g)}$ , and  $D_g$  illustrate that the phase boundary is the most prone to corrosion followed by the grain boundary, whereas the grain surface is relatively stable. Spinel particles fall off or react to completion, leaving holes in the silicon-rich phase (*cf.* Spinel II). The precipitation of sulfate may occur locally if the temperature is too high. Some of the inner spinel phase may react when the solution flushes the solid layer and is in direct contact with the spinel (*cf.* Spinel III); however, other deeper spinel phases cannot be leached over short times (*cf.* Spinel IV), as the silicon-rich phase acts as a barrier. The model developed by Zhao *et al.* is based on the experimental results of leaching chromite lump, and the sulfuric acid leaching behavior of the chromite with the optimized particle size should be further studied.



Figure 3. Leaching mechanism of chromite with sulfuric acid [57].

Although by using an appropriate oxidant the extraction of chromium can exceed 90% under optimal conditions, further studies are required to explore the choice of oxidant and its amount, revealing the mechanisms governing chromite spinel decomposition at a microscopic level.

## 4. Separation of Cr<sup>3+</sup> and Fe<sup>3+</sup> in Sulfuric Acid Leaching Solution

The main components in the sulfuric acid leaching solution of chromite are the sulfates of chromium, ferrous, aluminum, and magnesium. The ionic radius of  $Cr^{3+}$  and  $Fe^{3+}$  (0.62 and 0.64 Å, respectively) are so close that good separation of  $Cr^{3+}$  and  $Fe^{3+}$  is difficult to achieve. In contrast,  $Al^{3+}$  and  $Mg^{2+}$  are relatively easier to remove from the solution. Chromium salt products have strict limits on the impurity content of iron. The Chinese chemical industry standard (HG/T 267895) requires the ferrous content to be <0.1% in industrial basic chromium sulfate, and the Russian standard (FOCT2912-79) limits FeO content to below 0.01% [59]. Hence, one of the most important reasons for the failure of the sulfuric acid leaching process at industrial scale is the difficulty of separating  $Cr^{3+}$  and  $Fe^{3+}$  [60]. A significant number of studies have been carried out, and substantial progress has been made in the development of separation technology for  $Cr^{3+}$  and  $Fe^{3+}$  in the sulfuric acid solution. Some of this research is described in more detail in the following section.

## 4.1. Separation by Solvent Extraction

#### 4.1.1. Liquid-Liquid Extraction of Chromium

In 1977, Stauter *et al.* [61] successfully separated  $Cr^{6+}$  and  $Fe^{3+}$  in sulfuric acid leaching solution by using the liquid-liquid extraction method. As the separation of  $Cr^{3+}$  and  $Fe^{3+}$  is much more difficult, later investigation [53] indicated that  $Cr^{3+}$  could be extracted into the organic phase, and thus  $Cr^{3+}$ and  $Fe^{3+}$  could be separated in the presence of primary amine (R, R'–CH–NH<sub>2</sub>) as the extractant. After stripping by sulfuric acid, the separation coefficients of chromium and iron were >200.

## 4.1.2. Liquid-Liquid Extraction of Iron

Akash *et al.* [62] investigated the separation efficiency of  $Fe^{3+}$  from the  $Cr^{3+}$ -bearing solution and reported Cyanex923 as an effective extractant. Shi *et al.* [63] extracted  $Fe^{3+}$  from the  $Cr^{3+}$ -bearing solution using octadeyl dimethyl tertiary amine as the extractant. Ma *et al.* [64] extracted  $Fe^{3+}$  from the  $Cr^{3+}$ -bearing solution using bis(2-ethylhexyl) phosphoric acid (D2EHPA) as the extractant. After the extraction, the ferrous form was stripped from the organic phase by hydrochloric acid.

The prominent advantage of the solvent extraction method is its economical basis, because the extractant can be recycled. However, the expectation for sufficiently high removal efficiency of iron with a very low loss of chromium is difficult to achieve.

## 4.2. Recovery of Chromium by Salting-Out

In the mixed system of organic phase (water-soluble) and water, the solubility of the purple salt  $([Cr(H_2O)_6]_2(SO_4)_3)$  is much smaller than that of ferric sulfate. This property is utilized for salting-out chromium from the mixed solvent to separate chromium and iron. Wei *et al.* [65] used this method to separate chromium from iron in the leachate of ferrochromium alloy and the results showed that almost all  $Cr^{3+}$  was converted to  $[Cr(H_2O)_6]_2(SO_4)_3$ . After the addition of ethanol to the leachate and vibration for a period of time, the purple salt precipitated. Chromium sulfate was obtained after drying in 97.1% purity.

## 4.3. Removal of Iron by Precipitation Methods

To improve the separation, different precipitation methods for iron or chromium have been proposed.

## 4.3.1. Iron Hydrolysis

The pH value is different when hydrolysis reactions of different metal ions are at equilibrium. Compared to other metal ions, dissolved iron is more prone to hydrolyze and precipitate as ferric hydroxide Fe(OH)<sub>3</sub> [66]. Souza *et al.* [67] used hydrochloric acid to dissolve electroplating sludge and obtained an acid leaching solution containing  $Cr^{3+}$ , Fe<sup>3+</sup> and other metallic ions. After the addition of H<sub>2</sub>O<sub>2</sub> to the solution,  $Cr^{3+}$  was oxidized to  $Cr^{6+}$ . Then, by adjusting the pH value, Fe<sup>3+</sup> and other metal ions (except  $Cr^{6+}$ ) precipitated in the form of hydroxides. Because of the strong adsorption by Fe(OH)<sub>3</sub>, the concentration of iron in the solution was very low, and the loss of chromium decreased to ~8%.

When the concentration of  $Fe^{3+}$  is sufficiently low,  $Fe^{3+}$  can be precipitated as goethite (FeOOH) by adjusting the pH value [68,69]. The chemical reaction is shown in Equation (4).

$$Fe^{3+} + 2H_2O = FeOOH \downarrow + 3H^+$$
(4)

Chen *et al.* [70] carried out an experimental study on iron removal from the sulfuric acid leaching solution of chrome cake using the goethite process. Oxygen was blown into the leaching solution, and the oxidation rate was controlled by tuning the rate of oxygen addition. The concentration of Fe<sup>3+</sup> in solution was controlled to  $<1.5 \text{ g} \cdot \text{L}^{-1}$  during the entire process. The iron removal was 99.5%, but the total chromium loss reached 17%. Hu *et al.* [71] controlled the oxidation rate of Fe<sup>2+</sup> in the leachate of ferrochromium alloy by injecting H<sub>2</sub>O<sub>2</sub> slowly to ensure that the concentration of Fe<sup>3+</sup> was  $<1.0 \text{ g} \cdot \text{L}^{-1}$ . Finally, the removal of iron reached 99%, and the chromium loss was 15%. The above studies indicate some limitations to the oxidation rate of Fe<sup>2+</sup> to ensure that the concentration of Fe<sup>3+</sup> is maintained at a low level. To control the concentration of Fe<sup>3+</sup> at  $<1.0 \text{ g} \cdot \text{L}^{-1}$ , the production efficiency of goethite becomes low. In addition, the chromium loss is usually >15% because of the strong adsorption by goethite at the pH values used to form goethite.

## 4.3.2. Jarosite Process

According to the equilibrium diagram for the Fe<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O system [68], by adjusting the pH value and temperature, Fe<sup>3+</sup> can be precipitated from the sulfate solution in the form of a basic salt, normal salt or acidic salt. Among these salts, the basic salt ( $3Fe_2O_3 \cdot 4SO_3 \cdot 9(H_2O)$ ) is the most stable and can also be written as  $(H_3O)_2 \cdot 3Fe_2O_3 \cdot 4SO_3 \cdot 6H_2O$ . When Na<sup>+</sup>, K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> is present in the solution,  $(H_3O)_2 \cdot 3Fe_2O_3 \cdot 4SO_3 \cdot 6H_2O$  can be transformed into jarosite analogs (Na,K,NH<sub>4</sub>)<sub>2</sub>Fe<sub>6</sub>(SO<sub>4</sub>)<sub>4</sub>(OH)<sub>12</sub>, which are usually very stable. The reaction is shown by Equation (5) [72].

$$3Fe_2 (SO_4)_3 + 12H_2O + Na_2SO_4 = Na_2Fe_6 (SO_4)_4 (OH)_{12} \downarrow + 6H_2SO_4$$
(5)

Zhang [73] combined the goethite and jarosite processes to separate Fe<sup>3+</sup> from the Cr-rich solution from chromite at room temperature and atmospheric pressure. The ferrous removal reached 97%, while the loss of chromium was 15%. Shi [74] studied the ferrous removal from chromite leachate using the jarosite process under hydrothermal conditions in an autoclave. The ferrous removal was >99% and, at the same time, the chromium loss was 5.9%.

## 4.3.3. Formation of Mohr's Salt

The principle of Mohr's salt process is to crystallize ammonium chromium sulfate and ammonium ferrous sulfate (Mohr's salt) by adding ammonium sulphate into the solution containing  $Cr^{3+}$  and  $Fe^{2+}$ . The crystallization reactions are shown in Equations (6) and (7).

$$FeSO_4 + (NH_4)_2 SO_4 + 6H_2O = Fe(NH_4)_2 (SO_4)_2 \cdot 6H_2O$$
(6)

$$Cr_{2}(SO_{4})_{3} + (NH_{4})_{2}SO_{4} + 12H_{2}O = Cr_{2}(SO_{4})_{3}(NH_{4})_{2}SO_{4} \cdot 12H_{2}O$$
(7)

When the temperature is 0 °C, the solubility of ammonium ferrous sulfate is 0.4 g· L<sup>-1</sup>, and the solubility of ammonium chromium sulfate is 70 g· L<sup>-1</sup>. The difference in the solubility can be used to precipitate ferrous to remove iron from the solution. Some researchers [75–77] carried out ferrous removal experiments from the sulfuric acid solution of ferrochromium alloy by using the Mohr's salt process. The concentration of ferrous ion was decreased to ~0.1 g· L<sup>-1</sup>, and the ferrous removal tops out at ~95%. Because of the theoretical limitation of this method, ferrous ions cannot be precipitated completely; therefore, clean separation is hard to achieve.

#### 4.3.4. Ferrous Oxalate Precipitation

Ferrous oxalate precipitates can be formed by adding oxalic acid into the Fe<sup>2+</sup>-bearing solution. The reaction is shown in Equation (8).

$$Fe^{2+} + H_2C_2O_4 = FeC_2O_4 \downarrow + 2H^+$$
 (8)

Hu [78] and Wang [79] both studied the removal of  $Fe^{2+}$  from a leachate of carbon ferrochrome by ferrous oxalate precipitation. The content of chromium in the ferrous oxalate product was very low. However, the ferrous removal was not satisfactory and the content of ferrous in chromium oxide powders was up to ~0.5%. Moreover, the oxalic acid is expensive, increasing the process cost.

As mentioned above, the separation of iron and chromium has been improved through on-going efforts. As a result, a clean hydrometallurgical process can be designed, taking the preparation process of basic chromium sulfate as an example [80]. As shown in Figure 4, chromite is first decomposed by sulfuric acid solution with the addition of an oxidant, and  $Cr^{3+}$  is extracted into the acid solution. The major component of the residue is SiO<sub>2</sub>, which can be directly applied to ceramic preparations and in the construction industry. For the removal of iron, seed crystal is added to the acid solution, and jarosite is precipitated by the hydrothermal treatment, which can be used for the preparation of pigment and magnetic material. Notably, jarosite is potentially unstable and can be releached under suitable conditions if not impounded correctly. After the removal of iron, basic chromium sulfate is obtained by adjusting the basicity of the solution by adding sodium carbonate followed by drying. Some preliminary experimental studies have shown that no hexavalent chromium is generated in the entire process. Moreover, the mass fraction of iron in the basic chromium sulfate is <0.1% [75]. However, the chromium loss is also high ( $\geq 4\%$ ).



Figure 4. Process flow chart for the production of a chromium salt from chromite ore.

## 5. Conclusions and Perspectives

Because of the acute toxicity of Cr(VI)-bearing substances, the pollution problem caused by the residue from the preparation process of chromium salts with chromite as the raw material has become a worldwide concern. For the development of a clean hydrometallurgical process of chromite, a large number of studies focusing on the fundamentals and technology developments have been conducted. Although a significant progress has been made, the technologies based on the alkali treatment cannot fundamentally resolve the pollution problem because they require the oxidation of Cr(III) to Cr(VI).

As Cr(III) is soluble in sulfuric acid solution as chromium sulfate, oxidizing Cr(III) to Cr(VI) is not required in the sulfuric acid treatment process of chromite. The Cr(VI) pollution can therefore be eliminated from the original source of production. With the on-going efforts, the resolutions of the key obstacles hindering the development of the sulfuric acid treatment process have achieved significant progress. A clean hydrometallurgical process without hexavalent chromium is demonstrated in this study. First, the chromite is decomposed in sulfuric acid solution with oxidation, and  $Cr^{3+}$  is extracted into the acid solution. Seed crystal is added to acid solution, and the jarosite is precipitated by the hydrothermal treatment. After the removal of iron, the basic chromium sulfate is obtained by adjusting the basicity of the solution with sodium carbonate, separation, and drying. This clean technology for the preparation of chromium salts based on the sulfuric acid leaching process is believed to be suitable for commercialization, achieving industrialization in the near future.

This study, focused on the leaching of chromite in sulfuric acid, achieved chromium extractions exceeding 90% under optimal conditions, and the thermodynamic and kinetic mechanisms of chromite spinel decomposition were clarified. To further improve the extraction of chromium, more studies are required to explore the choice of oxidant and its amount with the premise that no Cr(VI) is generated. Furthermore, jarosite is potentially unstable and subsequent chromium loss is high in the iron removal process; therefore, further study is required to impound jarosite correctly, minimizing the chromium loss. Finally, to obtain a detailed and thorough assessment of the economical efficiency and potential for contamination, scaled-up test work should be carried out.

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