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New strategy in Chromium extraction: high efficiency without Chromium

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ABSTRACT

Chromium (Cr) is a very important metal. In nature, Cr is present in chromium ores and the most important part is chromite. Chromite processing is done using pyrometallurgical and hydrometallurgical technologies. Pyrometallurgical technology is generally done by extracting Cr into Fe and chromium alloys called FeCr and other alloys, while hydrometallurgical technology is generally done by extracting Cr into chromite oxide. In general, Cr extraction is done by 2 methods, namely aluminothermic and electrolytic methods. This shows that Cr metal is obtained through hydrometallurgical technology which is then carried out with pyrometallurgical technology in the aluminothermic process. The latest Cr extraction technology generally uses slag or waste that still contains Cr. Based on considerations regarding the increase in Cr extraction and Cr(VI) produced, the most appropriate method is liquid phase oxidation in chromite ore leaching because it is able to produce Cr extraction up to 96% without producing chromite ore processing residue (COPR) containing Cr(VI), making it possible to utilize COPR directly.

Keywords: chromium ore; pyrometallurgy; hydrometallurgy; ferrochromium; hexavalent chromium.

INTRODUCTION

The element Cr was first identified in 1979 by the French chemist Louis Vauguelin (Morning, 1977) with atomic number 24 and atomic weight 51.996 (Rollinson, 1973). Chromite ($FeCr_2O_4$) belongs to the spinel group and is the main chromium-producing mineral. Chromite is usually found in ultrabasic rocks such as peridotite and dunite, as well as in stratiform and podiform deposits. The results of SEM analysis of chromite are shown in Figure 1. Qualitative EDAX analysis of the spinel grains showed a relatively unvaried composition dominated by Cr, Mg, Al, and Fe elements. This composition implies that the spinel grains are part of the solid solution continuum among the $FeCr_2O_4$-$MgCr_2O_4$-$FeAl_2O_4$-$MgAl_2O_4$ end members. There may also be some Fe^{3+} present in the chrome-rich spinel grains (as a component of oxidized

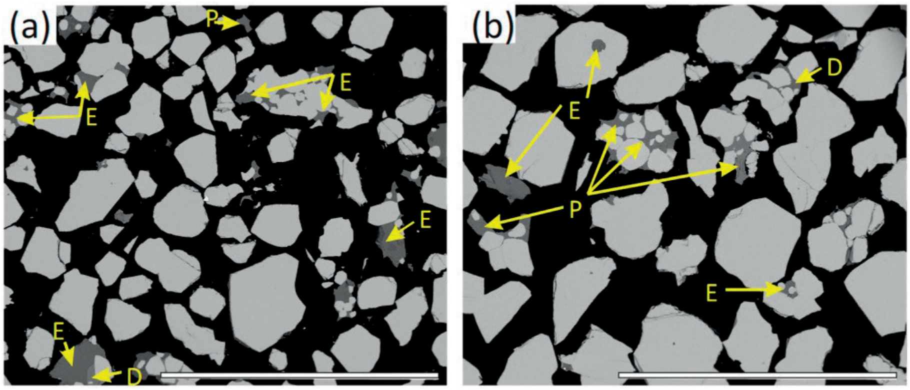

Figure 1. BSE images of (a) -2 mm bulk sample and (b) -600+425 μm fraction with E=enstatite, P=plagioclase (anorthite-rich), and D=diopside, while the bright grains are chromite.

magnetite spinel, Fe_3O_4) (Pownceby et al., 2023).

Production of chromite in China is highly dependent on imports because domestic sources of chromite are very scarce (Wu et al., 2019). Cr is a very important metal (Kreiner et al., 2022). The physical and chemical properties of Cr are as follows:

1. Specific gravity of Cr is 7.20 mg/l at 28 ºC
2. The melting point of Cr is 1837-1877 ºC
3. The boiling point of Cr is 2672 ºC
4. Ionization energy of Cr is 652 kg/mol
5. Cr is insoluble in dilute sulfuric acid and hydrochloric acid
6. Cr is immiscible with halogen peroxides, oxidizing bases, or other metals (Nurwati, 2009).

Chromite ore in various countries of the world is used in several different applications. In the United States, chromite ore is used in metallurgical (59%), refractory (20%), chemical (20%), and other applications (1%) (Morning, 1978). Meanwhile, applications of chromite ore in Japan include ferrochromium (90%), refractories (6%), chromium compounds (3%), and Cr metal (1%) (IARC, 1980). Cr is widely used for industrial applications (Pinto et al., 2019), chromium plating (Pianta et al., 2018), construction (Tasnim and Khajavi, 2022), health (Abdelkader et al., 2021), refractory materials, chemical industry, and metallurgy (Zhao et al., 2018; Tian et al., 2022). A very important part is chromite (Kumar et al., 2021). In metallurgical applications, chromite is converted to FeCr (Yu and Paktunc, 2018). One of the applications of Cr where it cannot be substituted by other elements is in the production of stainless steel (Kreiner et al., 2022). Cr applications include the manufacture of ferrochromium (95.2%), casting (2.4%), chemicals (1.6%) and refractories (0.8%) (Lunk, 2015). In the 1970s, most of the chromite ore producing countries produced FeCr alloy as a raw material (Papp, 1993). Other forms of chromium compounds are Cr(IV) oxide (CrO_2) which is ferromagnetic at room temperature and is a good conductor of electricity (Chamberland, 2017). Some companies that use Cr as an industrial material can be seen in Table 1.

The three chemical characteristics of Cr are as follows:

1. The predominant natural form of Cr is trivalent oxide. Cr can exist in every oxidation state from -2 to +6. The chromite mineral has a spinel crystal structure containing trivalent Cr, iron and small amounts of other divalent and trivalent metal oxides such as aluminum and magnesium with a very stable structure (Barnhart, 1997) $(Fe,Mg)[Cr,Al,Fe]_2O_4$ (Antony et al., 2001) which indicates that chromite mineral is a solid solution of $FeCr_2O_4$, Fe_3O_4, $FeAl_2O_4$, $MgCr_2O_4$, $MgFe_2O_4$, and $MgAl_2O_4$ (Tathavakar et al., 2005).
2. In nature, other forms will tend to change into trivalent oxide.
3. In a thermodynamically unstable environment, trivalent chromium oxide reacts very slowly (Barnhart, 1997).

Cr (III) is a biogenic element needed by animals (Fisinin et al., 2019). This form has very low solubility and low reactivity, resulting in low mobility in the environment and low toxicity to living organisms (Barnhart, 1997). Cr (III) deficiency can lead to heart problems, metabolic dysfunction, and diabetes. One of the primary metals that pollute the environment is Cr(VI). Symptoms of Cr (VI) poisoning in plants include decreased germination, decreased growth, inhibition of enzymatic activity, impaired photosynthesis, and oxidative imbalance (Ertani et al., 2017; Daud et al., 2021). Organisms can become

Table 1. The industrial named in Indonesia.

Company	Field
PT. Trimulyo Kencana Mas Semarang	Leather industry
PT. Elco Indonesia Sejahtera	Leather tanning
PT. Samwoo Indonesia	Leather tanning
PT. Jannas	Leather industry
PT. Adi Satria Abadi	Leather tanning
PT. Kasin	Leather tanning
PT. Tong Hong Tannery	Leather tanning
PT. Garut Makmur Perkasa	Leather tanning
PT. Budi Makmur Jaya Murni	Leather tanning
PT. International Leather Works	Leather tanning
PT. Elektroplating Superindo	Metal surface coating
PT. Indo Kida Plating	Electroplating
PT. Golden Kurniatama	Electroplating
PT. Asmar Nakama Partogi	Electroplating
PT. Cipta Kreasi Metal	Electroplating
PT. Enkei Indonesia	Electroplating
PT. Murni	Electroplating
PT. Insoclay Acidatama Indonesia	Electroplating

contaminated with Cr(VI) through soil, surface water and groundwater. For example, potassium chromate (K_2CrO_4) can enter the bloodstream through a break in the skin resulting in blood poisoning when CrO_4^{2-} destroys red blood cells (Jacobs and Testa, 2016). Therefore, minimizing waste from the chromium extraction process is crucial, particularly due to the environmental hazards posed by Cr(VI), which is especially problematic in countries with limited Cr reserves. To address this, various conventional and non-conventional methods have been developed, emphasizing the need for innovative, cost-effective, and environmentally friendly technologies. These strategies aim not only to reduce toxic emissions but also to enhance Cr recovery efficiency, which will be further discussed in the context of both pyrometallurgical and hydrometallurgical advancements.

CHROMIUM EXTRACTION TECHNOLOGY

Pyrometallurgy

Cr extraction was carried out using pyrometallurgical and hydrometallurgical technology. Pyrometallurgical technology can produce metals using a coke reducing agent with a chemical reaction as in Eq. 1 (Yang et al., 2004).

$$FeCr_2O_4+4CO_{(g)}\rightarrow 2Cr+Fe+4CO_2(g) \quad 1)$$

Under reducing conditions, the alkali complexes with chromium oxide in the 3+ state and forms water-insoluble sodium chromite ($Na_2O{\cdot}Cr_2O_3$). The reaction that occurs in the reductive roasting of chromite ore with alkali is shown in Eq. 2-9 (Escudero-Castejon et al., 2021).

$$FeCr_2O_4+Na_2CO_3+2C=Fe+Na_2Cr_2O_4+3CO_{(g)};\Delta G^o=466.491-44.3T \quad (2)$$

$$Al_2O_3+Na_2CO_3+C=2NaAlO_2+2CO_{(g)};\Delta G^o=337267-287.2T \quad (3)$$

$$Na_2CO_3+SiO_2+C=Na_2SiO_3+2CO_{(g)};\Delta G^o=284162-299.0T \quad (4)$$

$$MgCr_2O_4+Na_2CO_3+C=MgO+Na_2Cr_2O_4+2CO_{(g)};\Delta G^o=321105-289.2T \quad (5)$$

$$FeAl_2O_4+Na_2CO_3+2C=Fe+2NaAlO_2+3CO_{(g)};\Delta G^o=313087-286.4T \quad (6)$$

$$MgAl_2O_4+Na_2CO_3+C=MgO+2NaAlO_2+2CO_{(g)};\Delta G^o=315522-285.2T \quad (7)$$

$$MgSiO_3+Na_2CO_3+C=MgO+Na_2SiO_3+2CO_{(g)};\Delta G^o=268000-287.4T \quad (8)$$

$$CaO.Al_2O_3.2SiO_2+3Na_2CO_3+3C=2Na_2SiO_3+2NaAlO_2+CaO+6CO_{(g)};\Delta G^o=207880-205.5T \quad (9)$$

The reaction mechanism is that the iron oxide present in spinel chromite is reduced to metallic form by forming Fe-Cr alloy above 1173K (900 °C), which can be magnetically separated from the non-magnetic phase, while alumina forms $NaAlO_2$ and silica forms water-soluble Na_2SiO_3. Thus the water-insoluble sodium chromite can be separated during leaching from $NaAlO_2$. The remaining oxides, MgO, Al_2O_3 and silica form complex silicates during leaching. The reduction reaction produces CO gas which can be used for combustion to produce energy. The CO_2 gas generated from the combustion of CO gas will be used for the recovery of Na_2CO_3 to be reused in the process (Escudero-Castejon et al., 2021).

Pyrometallurgical technologies that can be used are SBS-SAF, RK-SAF, shaft furnace (SF) (Hamuyuni et al., 2021), *electric arc furnace argon oxygen decarburization* (EAF AOD) (Wang et al., 2020; Gu et al., 2021), and converter technology (Yan et al., 2021). In SBS-SAF technology, chromite concentrate pellets are melted in SAF with a series of processes (Basson and Daavittila, 2013). The stages of the sintering process in SBS-SAF technology consist of 4 stages, namely drying (350-400 °C), heating (1050-1100 °C), sintering (1300 °C), and cooling. Furnace gas heat and exhaust gases and coke burning are the energy supplies for this process (Hekkala et al., 2004; Basson and Daavittila, 2013; Yu et al., 2021). This technology is widely used in China because it is a mature technology, compared to RK-SAF (Rong et al., 2017). In RK-SAF technology, pellets containing water are dried and preheated using flue gas and burning bituminous coal to evaporate the water contained in the pellets. Furthermore, sintering and pre-reduction of the pellets is carried out in the rotary kiln before melting. Pre-reduction has a positive impact because it can reduce energy consumption in SAF during smelting (Naiker, 2007; Basson and Daavittila, 2013; Eric, 2013; Yu et al., 2021).

EAF-AOD technology is performed on Cr smelting (70% stainless steel smelting). EAF is used to melt scrap steel and its alloys to form molten metal, while AOD is for decarburization and prevention of Cr oxidation. Slow cooling rates can reduce Cr(VI) emissions in stainless steel slag (Li and Xue, 2019). The production of FeCr, FeNi, and stainless steel produces slag containing magnesium, silica, alumina, Cr_2O_3, calcium oxide (CaO), and iron oxide (Daud et al., 2021). These compounds are potential materials that can still be reused (Jacobs and Testa, 2016). Another product is ferrosiliconchrome (FeSiCr) alloy (Zou et al., 2013; Xu et al., 2015). This alloy is used in steelmaking or as a reducing agent in low carbon (<0.03% C) FeCr processing. The process of making this alloy is by reducing silicon from quartzite by carbon (coke) and the presence of high carbon FeCr (unreduced Cr), then adding chromite ore so that Cr and Si are reduced simultaneously by carbon (Gasik, 2013). In addition, FeSiCr can also be used as a multilayer inductor (Wu and Hsiang, 2022). In SF Technology there are processes of smelting or calcination or roasting. This tool is in the form of a cylindrical or rectangular shaft through which solid material flows downwards into an empty space. The fuel used in this process is coke. One of the most developed forms of SF is the iron blast furnace (Gilchrist, 1977). However, this technology has weaknesses, namely capacity and pre-reduction rate as a pellet production unit (Hamuyuni et al., 2021).

In recent years, smelting of chromite ore into raw molten stainless steel uses converter technology that uses cheap chromium ore powder to increase the flexibility of the main raw material (Yan et al., 2012). Steelmaking using converters produces converter exhaust gas and dust which pollutes the environment. Therefore, a recycling process is carried out by utilizing CO_2 gas from steel production effectively (Zhou et al., 2022). Oxygen converter technology is a technology that is widely used to produce high-grade steel. The reason is the higher decarburization rate compared to EAFs with the same inner diameter of the unit (Wallner and Fritz, 2002).

In the conventional Cr extraction process, CaO and Na_2CO_3 are used as fluxes in the oxidative roasting of chromite ore. The purpose of this process is to convert Cr(III) to Cr(VI) in the form of chromate (CrO_4^{2-}), which is soluble in water and can be separated from impurity minerals. The main reaction is shown in Eq. 10 (IARC, 2012).

$$4FeCr_2O_4+8Na_2CO_3+7O_2 \rightarrow 8Na_2CrO_4+2Fe_2O_3+8CO_2 \qquad (10)$$

However, the process was abandoned because it produces calcium chromate which is carcinogenic and its presence in the form of aerosols or gases is very difficult to control in industrial environments (IARC, 2012).

Pyrometallurgical technology for processing chromite ore can cause climate change, acidification, particles, and use of resources (minerals and metals) (Hamuyuni et al., 2021). This activity can also increase Cr(lll) levels in air and stainless steel welding activities can increase Cr(VI) levels in air (Roper, 2012). One of the causes of the release of Cr(VI) in nature is the processing of chromate ore at high temperatures (Laxmi and Kaushik, 2020). Highly toxic Cr(VI) element (Ertani et al., 2017; Daud et al., 2021) it can contaminate agricultural land (Umer et al., 2021) and in the aquatic environment (Huang et al., 2019) so that it can expose microorganisms, plants, animals, and humans (Rahman and Singh, 2019; Wu et al., 2019). Therefore, chromate forming processes are no longer recommended, and have been replaced by alternative technologies using hydrometallurgical technologies, such as reductive alkali roasting to avoid the formation of Cr^{6+} altogether (Escudero-Castejon et al., 2021).

Hydrometallurgy

Hydrometallurgical technology is carried out to increase the efficiency of Cr extraction (Matern et al., 2020; Yan et al., 2021) by producing Cr_2O_3 which is inorganic through hydrometallurgical technology and is widely used in metallurgy (Escudero-Castejon et al., 2021), chemical industry, and other industries which account for about 15% of China's national economic variety of commodities (Zhao et al., 2020). Industrial production of Cr_2O_3 is generally obtained by a lime-based baking process (Parirenyatwa et al., 2015) and without lime (Du and Chrysochoou, 2020) which is dangerous because the COPR produced contains calcium chromate ($CaCrO_4$) (Zhao et al., 2020). Generally, Cr extraction is carried out by 2 methods, namely aluminothermic and electrolytic methods (Zhao et al., 2018). The aluminothermic method involves processing Cr ore into chromate oxide (made from sodium dichromate), which is then processed into Cr metal. Meanwhile, the electrolytic method is done by processing chromium ore into ferrochromium, then into Cr metal (Manly et al., 1995). The flow diagram of the aluminothermic process in the production of chromium alloys and metal compounds and from chromite ore is shown in Figure 2. Hydrometallurgical technology generally processes chromite ore to produce Cr_2O_3, while the commercial production of Cr metal uses an aluminothermic process, namely using Cr_2O_3 powder and granulated aluminum which is mixed and heated in a smelting furnace (Langård, 1982).

This shows that Cr metal was obtained through hydrometallurgical technology which was then carried out by pyrometallurgical technology in an aluminothermic process. Ferrochromium is obtained by smelting chromite ore with coke at high temperatures (above 1600 °C), with pre-reduction of chromite in a partially solid state (Escudero-Castejon et al., 2017). Smelting at this temperature is because the melting point of iron is 1538 °C. A chemical reaction as in Eq. 11 (Escudero-Castejon et al., 2017).

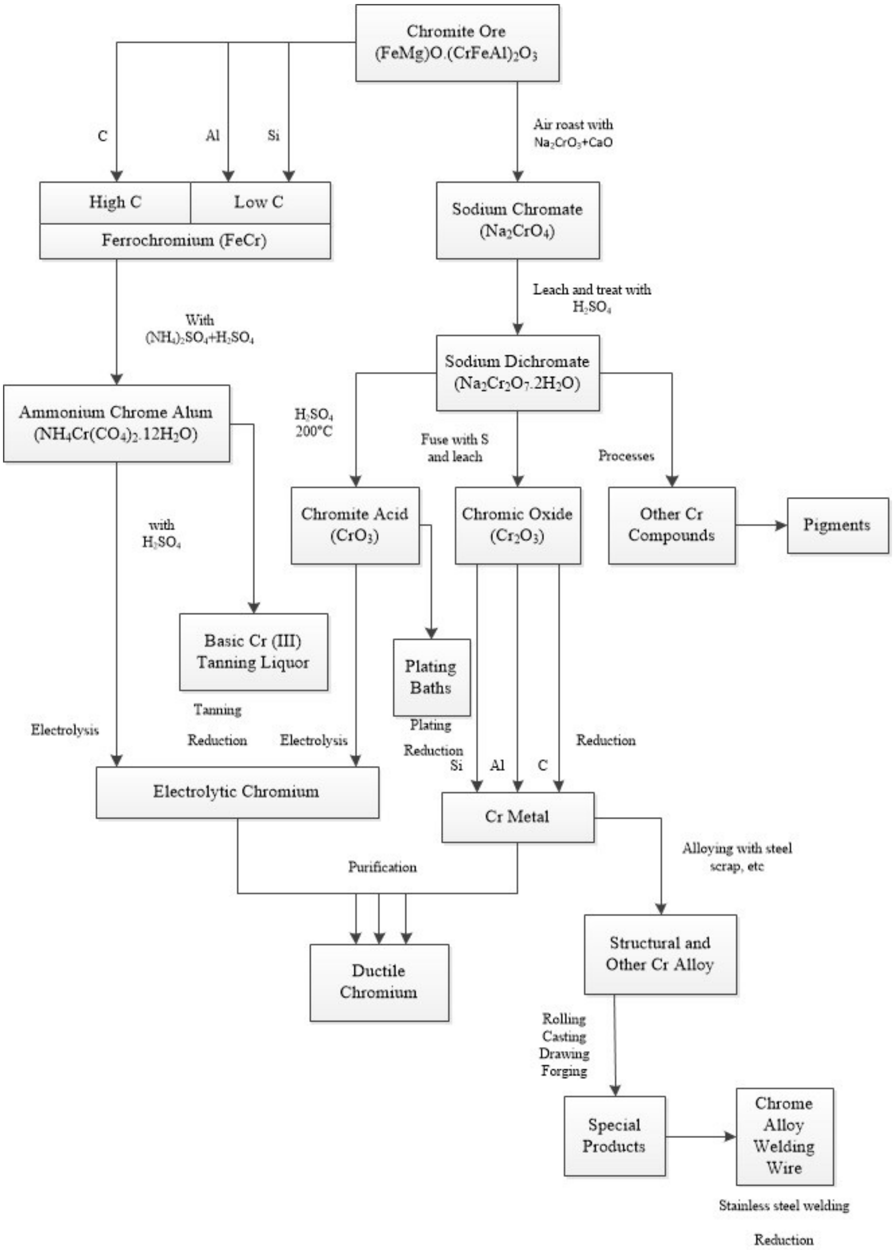

Figure 2. Flowchart of the aluminothermic and electrolytic process of chromite ore (Langard, 1982).

$Cr_2O_3+3[C]_{Fe}\leftrightarrow 2[Cr]_{Fe}+3CO_{(g)}$ (11)

However, the presence of CaO, MgO, and small amounts of oxygen in a high temperature furnace can catalyze the oxidation of Cr as shown in Eq. 12-13 (Berryman and Paktunc, 2022).

$2Cr_2O_3+3O_{2(g)}+4CaO=4CrO_4^{2-}+4Ca^{2+}$ (12)

$2Cr_2O_3+3O_{2(g)}+4MgO=4CrO_4^{2-}+4Mg^{2+}$ (13)

Based on the description above, the main problems faced from Cr extraction technology are causing greenhouse gas emissions and producing Cr(VI) which can pollute the environment because it is toxic. Therefore, some of the latest technologies are expected to overcome the problems caused by previously existing technologies.

THE LATEST TECHNOLOGY OF CHROMIUM EXTRACTION

The latest technology to overcome problems in Cr extraction is by replacing coke with biomass, increasing productivity through recovering Cr from slag, utilizing industrial waste that still contains Cr using several methods (adding alkali, separating Mg from the host phase Mg-Cr, and roasting Na_2CO_3), water washing, and so on), as well as conducting research methods that emphasize the removal of toxic Cr(VI) elements so as not to pollute the environment. Based on the results of the global climate conference, the main source of emissions is carbon dioxide (CO_2). Therefore, the use of carbon switch to green technology (Fu et al., 2014; Qiu et al., 2022) which is an important technology that can be used in industry because it can neutralize carbon, increase net output, and energy efficiency (Sharif et al., 2022). One application of green technology is to replace coal into biomass as a reducing agent (Zhang et al., 2021).

Research on the beneficiation of chromite sand before smelting in SAF was carried out by roasting chromite sand at 1000 °C (60 minutes) with a reducing agent, palm shell charcoal and magnetic separation again to produce FeCr with a Cr/Fe ratio from 0.9 to 1.6 as shown in Figure 3 (Nurjaman et al., 2018). High carbon content (Sari et al., 2024) and large specific surface area have a positive effect on the reduction of metal oxides to metals (Sari et al., 2024). However, an excessive amount of reductant can hinder the reduction rate due to the presence of impurities such as alumina, phosphorus, and quartz (Bahfie et al., 2022). The carboxyl (-COOH) and phenolic (-OH) groups contained in the biomass act as electron donors to reduce Cr(VI) to Cr(III) through redox reactions. This process also involves the consumption of protons (H^+) which causes a decrease in the pH of the solution during the reaction. The main redox reactions that occur during the reduction of Cr(VI) by biomass are shown in Eq. 14-15 (Huang et al., 2015).

$HCrO^{4-}+7H^++3e^-\rightarrow Cr^{3+}+4H_2O$ (14)

$Cr_2O_7^{2-}+14H^++6^{e-}\rightarrow 2Cr^{3+}+7H_2O$ (15)

In this reaction, the electrons required to reduce Cr(VI) to Cr(III) are provided by organic functional groups in the biomass (Huang et al., 2015). This mechanism is referred to as "adsorption-coupled reduction", where Cr(VI) is first adsorbed on the biomass surface and then reduced through interaction with functional groups (Vo et al., 2019).

Increasing the productivity of the process of smelting chromite ore to produce ferrochromium can be done by adding calcium chloride ($CaCl_2$). The results obtained can be seen in Figure 4 which illustrates a cross-section of the reduced product. The light gray part is the Cr-rich chromite core and the dark gray part is the spinel layer ($MgAl_2O_4$). Each chromite particle is partially reduced and finely dispersed in each chromite particle making it difficult to obtain high Cr gains through physical separation in Figure 4a. The degree of reduction is much

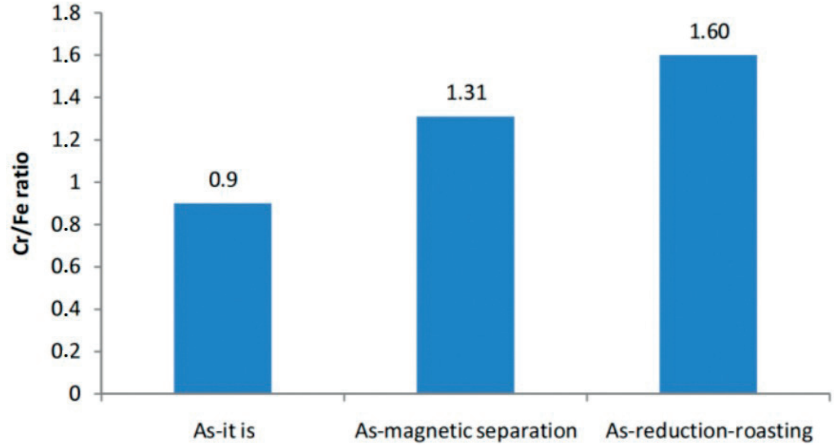

Figure 3. Cr/Fe ratio after beneficiation (Nurjaman et al., 2018).

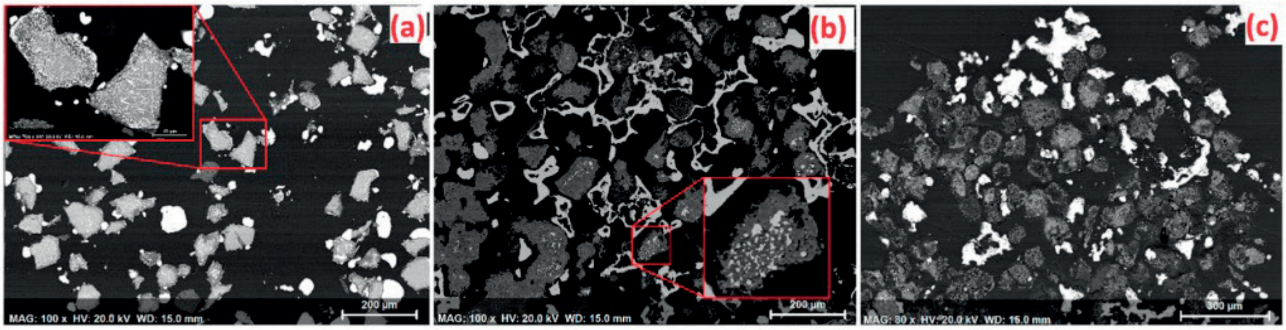

Figure 4. Reduced microstructure (a) without additives; (b) 10% by weight; and (c) 30% by weight addition of $CaCl_2$ (Yu and Paktunc, 2018).

higher (absence of a Cr-rich chromite core) and only a few fine FeCr particles are present (for example, the magnified particles in Figure 4b. The completely reduced chromite is characterized by $MgAl_2O_4$ and MgO is almost free. Based on the results of EDS analysis, reduced chromite particles contain an average of 1.1% by weight of Cr and 0.1% by weight of Fe, which means that the approximate degree of metallization is 98.9% by weight of Cr and 99.8% by weight of Fe in Figure 4c. It can be concluded that the addition of $CaCl_2$ was effective in promoting the formation of FeCr alloy particles (Yu and Paktunc, 2018). During the reduction process, the formation of a liquidus phase plays a crucial role in the migration and agglomeration of metallic particles. This phase can be promoted by modifying the basicity of the ore (binary, ternary, and quaternary systems) through the addition of low-cost fluxing agents such as CaO, SiO_2, MgO, and Al_2O_3 (Nurjaman et al., 2021; Nurjaman et al., 2021). Basicity modification through the addition of CaO can also reduce the activation energy (Suharno et al., 2023).

Alkali roasting of chromite ore with Na_2CO_3 at high temperatures (above 1100 °C) is used to oxidize Cr(III) to Cr(VI) in the form of water-soluble sodium chromate (Na_2CrO_4). However, the extraction efficiency of sodium chromate from chromite ore never reaches 100%, so the mineral residue always contains harmful Cr^{6+} ions (IARC, 2012). For example, the extraction efficiency of sodium chromate from South African chromite ore only reaches about 90%. This process residue, known as COPR, contains Cr^{6+} that can be released into the environment over time, especially through leaching by groundwater, posing a serious contamination risk (Moon et al., 2007).

COPR is a waste from chromate production which still contains about 10% Cr_2O_3. The method used to extract Cr is by selectively removing Mg by roasting $(NH_4)_2SO_4$ combined with washing sulfuric acid (H_2SO_4). The experimental results showed that the optimal conditions for the selective removal of Mg from COPR under optimal roasting conditions [80 mmol $(NH_4)_2SO_4$, temperature 800 °C for 2 hours] was 79.55% Mg. Washing with H_2SO_4 obtained a Cr extraction rate of 84.63% for COPR direct roasting and 95.39% for Mg removal residue roasting. This increase was due to the transformation of Mg-rich spinel and diopside (co-existent phases of Mg and Cr) in COPR into $(Fe,Cr)_2O_3$ and Cr_2O_3 after treatment of easily extractable Mg. Furthermore, extraction of Cr from COPR and active residue (AR) was carried out by roasting Na_2CO_3 and leaching process of H_2SO_4. First, COPR was mixed with Na_2CO_3 (dose from 0.5 g to 1.5 g) and baked in air at 1050 °C for 2 hours. The leaching residue was baked at 60 °C for 24 hours and named extract slag (ES). Meanwhile, the optimal roasting conditions for acidic AR and Na_2CO_3 with a mass ratio of 1:0.75 and acid washing for 6 hours produced a solid material and was named extraction residue (ER). The ratio of acidic AR and Na_2CO_3 was 1:0.75. This ratio is obtained by adding 2.0 g AR and 1.5 g Na_2CO_3. The mass of Na_2CO_3 used is the optimal mass obtained from the previous process, namely the ratio of COPR and Na_2CO_3 with the amount of COPR as much as 2.0 g and Na_2CO_3 as much as 1.5 g. The main phases of ES are Na_2AlFeO_4 (PDF# 30-1146), MgO (PDF# 43-1022), and $MgCrO\text{-}1Fe_{1.9}O_4$ (PDF# 71–1251). Meanwhile, ER only contains Na_2AlFeO_4 and Fe_3O_4 (PDF# 88-0315). The results showed that selective control and regulation can maximally remove Mg, thereby releasing the binding effect of coexisting Mg and Cr phases on Cr and effectively promoting sufficient Cr extraction in sodium baking (Zhang et al., 2022).

Another waste from the vanadium extraction process industry from vanadium slag and coal is chromium-containing vanadium tailings (CCVT) which can be processed for the preparation of pure Cr_2O_3 through the Na_2CO_3 water-roasting leach process. Optimal conditions at the molar ratio $[n(Na_2CO_3)/n(Cr_2O_3)]$ 8, baked at 900 °C for 120 minutes resulted in a Cr extraction rate of 91.51%. The addition of excess Na_2CO_3 can inhibit oxidation during roasting. Temperatures and roasting times that exceed the optimum can cause by-products to encapsulate the Cr phase which inhibits Cr extraction. During roasting (Na_2CO_3), the $(Fe_{0.6}Cr_{0.4})_2O_3$ phase reacts with Na_2CO_3 to form Na_2CrO_4. The unrefined washing liquid after reduction and precipitation by adding Na_2S (as a reducing agent for Cr(VI)) contains 87.40% Cr_2O_3. This process also produces waste that is acceptable to the environment because it contains concentrations of Cr(VI) and total Cr in the leaching fluids which are lower than 0.5 mg/L and 1.5 mg/L respectively. Furthermore, the Cr_2O_3 that had been obtained was subjected to XRD and SEM-EDS analysis. The Cr_2O_3 peak complies with the JCPDS standard: 01-082-1484. It can also be seen that there are a few impurities which are thought to be vanadium oxide, silicates, sodium salts, and so on. SEM micrograph with different magnifications. Most of the particulate matter is flat, and the particle size is small, even with nanoscale dimensions and the EDS analysis of the impurities present in the synthesized Cr_2O_3 (Wen et al., 2019).

Apart from chromite ore, Cr_2O_3 can also be extracted from COPR. Currently, there are two main methods to recover Cr from COPR namely washing and roasting methods (Jiang et al., 2014). The washing method uses an inorganic acid solution as a leaching agent. In COPR it was identified to contain Cr(III) and Cr(VI) (Kumar et al., 2021). So that COPR is considered as waste in the production of Cr where COPR still contains 10% by weight of Cr_2O_3 (Du and Chrysochoou, 2020). Cr element can also be extracted from vanadium tailings waste which is a by-product of the vanadium extraction process (Wei et al., 2017). Extraction of Cr from residues of nitric acid pressure leaching (NAPL) can also be carried out by metallization-magnetic separation reduction roasting using $CaCl_2$, in order to obtain Fe-rich concentrate and Cr-rich tailings (Long et al., 2016; Ma et al., 2017; Gao et al., 2018; Jin et al., 2021).

The smelting process of stainless steel and ferrochromium alloys produces solid waste in the form of chromium-containing dust and slag. Each ton of stainless steel production can produce about 300 kg of slag and 40 kg of dust. These wastes contain harmful elements, such as Cr, Pb, Ni, and Zn, which can pollute the environment if not managed properly (Xu et al., 2023). A composite agglomeration process (CAP) method that combines chromium slag and carbon-containing dust can be performed to produce composite pellets. These pellets are then used in a sintering and smelting process in a blast furnace, enabling the reduction of Cr(VI) to Cr(III) or Cr metal. The results show that this method can treat up to 20% chromium slag and 5% dust without compromising sinter quality, with Cr recovery rates reaching 90.22% after smelting (Tu et al., 2023).

Therefore, clean technology is a technology that does not produce waste that can pollute or damage the environment, such as the environmentally friendly monosodium glutamate, have shown promising results in selective metal extraction processes (Bahfie et al., 2022) and the calculation can be used Anova (Bahfie et al., 2022). The Cr processing industry produces Cr(VI) waste which is toxic. There are two ways to inhibit the formation of Cr(VI), namely with organic materials (Huang et al., 2019; Verdonck et al., 2019; Keshav and Kumar, 2020; Kushwaha et al., 2020) and inorganic materials (Almeida et al., 2019; Wu et al., 2019), etc. The liquid phase oxidation method of washing chromite ore is one method that can be used to obtain COPR waste without Cr(VI) content. In the liquid phase oxidation process, Cr in the form of Cr(III) is oxidized to Cr(VI) using a strong oxidizer in alkaline solution. This reaction follows the shrinking core model, with the rate-controlling step being the chemical reaction at the particle surface. The leaching process is controlled by surface chemical reactions with an activation energy of 34.31 kJ/mol. The flow chart of the liquid phase oxidation method for washing chromite ore can be seen in Figure 5. In the leached solution, Na_2CrO_4 is converted into $BaCrO_4$ by reaction with $Ba(OH)_2$, and the Cr separation efficiency reaches 89% in the undiluted concentrated solution. The residual alkaline solution can be recycled for the next leaching process. Finally, a new method for producing Cr_2O_3 from $BaCrO_4$ was introduced through a dissolution and reduction process using a mixture of HCl and ethanol (CH_3CH_2OH). Optimum conditions were obtained at reaction temperature 80 °C, reaction time 30 minutes, n(HCl)/n($BaCrO_4$) 4:1 mol/mol, liquid-solid ratio 6:1 mL/g, total CH_3CH_2OH added was 3 times the amount theoretically produces a conversion efficiency of Cr $BaCrO_4$ reaching 96%. This method has the advantage of not obtaining Cr(VI) from COPR which allows direct use of COPR, but produces $BaSO_4$. This new process offers an efficient and economical alternative to improve current methods of chromate salt production. Furthermore, the Cr_2O_3 product was subjected to XRD and SEM analysis. The peak position of Cr_2O_3 corresponds to the Cr_2O_3 standard (PDF#38-1479). There are no hetero peaks indicating the high purity of Cr_2O_3. The particle size of the synthesized Cr_2O_3 is mostly distributed in the range of 0.911-3.062 μm. The microstructure with a magnification of 20000 and 50000 times, which shows that most of the particulates are flat with very good uniformity, so they can be used as functional pigments (Tian et al., 2022). Total Cr after reduction and precipitation is environmentally acceptable (Wen et al., 2019). The limitation of this process is the use of expensive oxidizers, and it is not environmentally friendly because it introduces foreign ions into the system, making it difficult to separate and recycle the solution (Liu et al., 2022).

Based on the explanation of some of the technologies

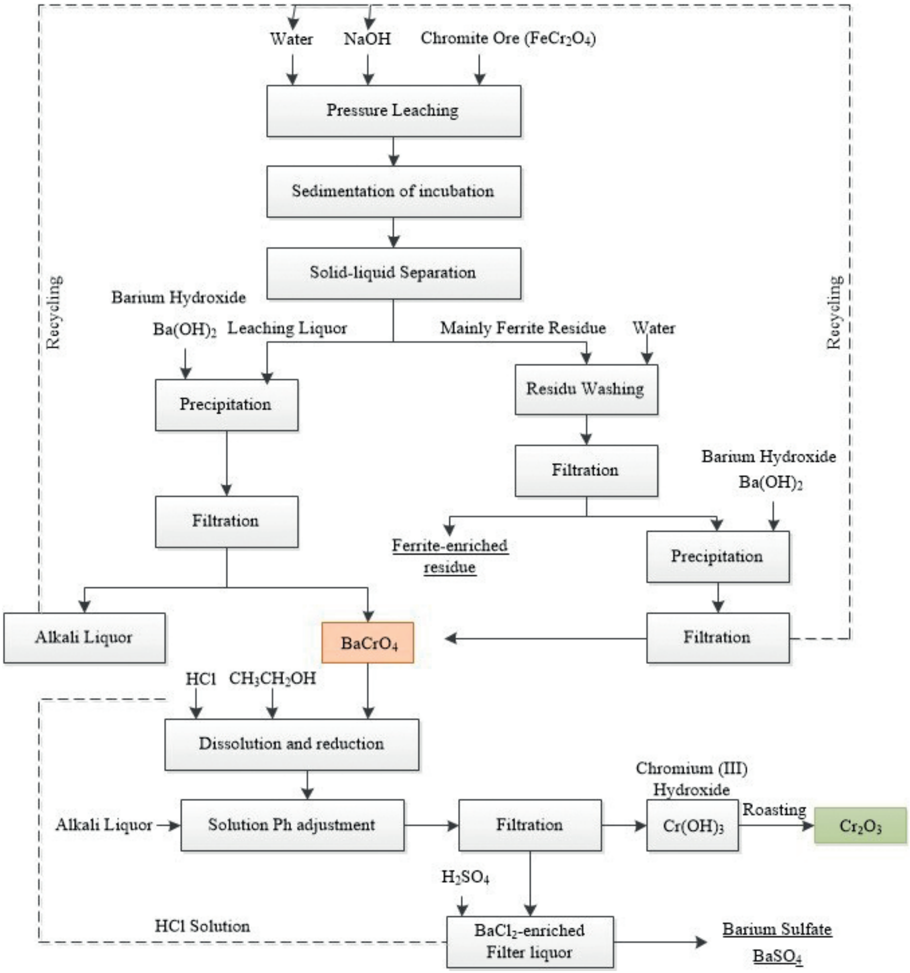

Figure 5. The flow chart of the liquid phase oxidation method (Tian et al., 2022).

above, it can be concluded that the advantages and disadvantages of these technologies can be seen in Table 2.

CONCLUSION

Chromite processing technology is carried out by pyrometallurgical technology to extract Cr into FeCr alloys and can also form other metal alloys, while hydrometallurgical technology is generally carried out by extracting Cr into Cr_2O_3. Chromite ore processing technology produces CO_2 emissions, slag which still contains magnesia, silica, alumina, Cr_2O_3, CaO, and iron oxide. In addition, Cr(VI) is also produced which is toxic and harmful to humans, animals, plants, and has a negative impact on the environment. The latest technology to overcome the above problems is by replacing coke with biomass, increasing productivity through recovering Cr from slag, utilizing industrial wastes that still contain Cr using several methods (adding alkali, separating Mg from the host phase Mg-Cr, and roasting Na_2CO_3 and water washing, and etc), as well as conducting research methods that prioritize the removal of toxic Cr(VI) elements so as not to pollute the environment. Based on considerations regarding the increase in Cr extraction and the resulting Cr(VI) waste, it is concluded that the most appropriate method for Cr extraction is oxidation of the liquid phase of washing chromite ore. Processing of chromite ore is carried out to produce Cr metal and its compounds which are then applied in different fields. The main area of application of Cr is in the manufacture of ferrochromium.

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Table 2. The advantage and disadvantages of Cr processing technology.

Technology		Environmental Impact	Economic Cost	Technical Efficiency	Quantitative Indicators
Pyrometallurgy	SBS-SAF	GHG emissions, Cr(VI) emissions, waste slag and dust containing Cr(VI)	Higher initial investment, lower operating cost per ton in the long run	Efficiency increased by utilizing heat from flue gas, consumption of reducing agent increased	Energy consumption 40-59 GJ/ton FeCr, CO_2 emissions 1.8-5.5 tons CO_2/ton FeCr, Cr content in HC FeCr 52%-69%, Cr(VI) concentration in BFD 150-340 mg/kg
	RK-SAF			Temperature distribution and gas flow, mass transfer	Energy efficiency 42.93%, exergy efficiency 30.7%, main exergy damage to AC circuit, medium energy saving potential
	EAF-AOD	Cr(VI) emission and slag stability, effect of cooling rate	Increased start-up costs for environmental cost reduction and improved process sustainability	Slag cooling rate regulation can improve technical efficiency in smelting process	Cr(VI) concentration in <0.01 mg/L, Cr distribution in spinel >99.9%
	Converter	Reduce GHG emissions and waste converter dust as well as Fe content in dust, integrate collection and recycling of dust from flue gas	More efficient process, reduced waste management costs, valuable metal recovery	The developed dynamic model incorporates the kinetics of chromium ore dissolution and the interfacial reduction reaction between slag and metal.	Average Cr reduction rate 0.091%/min, chromium ore injection rate 467 kg/min, reduction in dust production Top-blown CO_2-O_2: 9.95% and bottom-blown O_2-CaO 10.99%, reduction of Fe content in dust Top-blown CO_2-O_2 12.98% and bottom-blown O_2-CaO 16.58%.
Hydrometallurgy	Roasting	Preventing the formation of Cr^{6+} during the whole extraction process, the process is more environmentally friendly than conventional methods	Use of low quality raw materials, iron-rich fraction and alumina as by-products, reduction in waste management cost	Operating conditions 950-1050 °C, followed by magnetic separation and leaching, resulting in high purity Cr_2O_3 products, iron-rich magnetic fraction metal recovery, raw material flexibility	Operating temperature 950-1050°C, Reduction time 2.5 hours, Cr_2O_3 recovery about 85.6%, final product purity: about 83.6% Cr_2O_3, Cr^{3+} concentration in leach solution about 150 ppm
Current technology	Biomass utilization	More environmentally friendly approach, lower carbon emissions, reduced amount of waste, improved efficiency of raw material use	Raw material cost savings, trade-off between product quality and cost efficiency	Increased slag basicity decreased Cr recovery and increased specific energy consumption.	Cr/Fe ratio increased from 0.9 to 1.6 after beneficiation, reduction temperature 1000°C for 60 min, Cr recovery and specific energy consumption: decreased with the increase of slag basicity
	Addition of $CaCl_2$	Cr(VI) emission reduction, $CaCl_2$ reuse, SAF requirement elimination	Lower operating temperature at 1200-1400 °C, simple separation reducing processing costs, $CaCl_2$ recovery	Accelerated reduction, effective separation, high metal recovery	Operating temperature 1200-1400°C, $CaCl_2$ segregation catalyst, $CaCl_2$ consumption less than 10% and the rest can be obtained, lower specific energy consumption (SEC) than SAF
	Magnesium (Mg) separation method	Hazardous waste reduction, minimization of hazardous chemical use	Industrial waste utilization, waste treatment cost reduction	Improved extraction efficiency, mineral phase transformation	Roasting conditions 80 mmol $(NH_4)_2SO_4$, 800°C, for 2 hours, Mg removal efficiency 79.55% Mg from COPR, Cr extraction efficiency without Mg removal of 84.63% with Mg removal 95.39%
	Water leaching-roasting Na_2CO_3	Minimization of Cr(VI) formation, control of chromium sulfate precipitation	Use of common chemicals, optimization of process conditions	The effect of temperature and time can be: increase Cr extraction efficiency, sulfuric acid concentration of 80% and oxidizer to chromite mass ratio above 1:10, stirring affects the leaching reaction rate.	Optimal leaching temperature 160-180 °C, optimal sulfuric acid concentration 80% by weight, oxidizer/chromite ratio: above 1:10, optimal stirring speed 1800 rad/s
	Liquid phase oxidation method	Reduction of Cr(VI) formation, utilization of hazardous waste	Use of secondary raw materials, process efficiency	Impurity removal, chromite stability	High chromium extraction efficiency, high purity Cr_2O_3 end product, Cr(VI) emission concentration: expected to be very low or undetectable
	CAP-BF Method	Cr(VI) effluent reduction, emission reduction, solid waste utilization	Operational cost efficiency, waste treatment cost savings, infrastructure investment	Agglomerate stability, furnace reactivity, Cr(VI) reduction, suitability for blast furnace process	Initial Cr(VI) level ~9300 ppm, reduction efficiency of Cr(VI) to Cr(III) >99%, residual heavy metal content below hazardous waste standard limit, cold compressive strength >2000 N (sufficient for blast furnace application), operating temperature 1250-1350°C, waste utilization ratio >70%.

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