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The Preparation of Inorganic Materials to Consume and Stabilize Chromium-Containing Waste: A Review

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Currently, a large amount of chromium-containing solid waste (CCSW) is still accumulating, and has caused a series of ecological problems that are difficult to solve. Inorganic materials have been extensively studied for their capability to consume CCSW. This paper reviews the research on four groups of inorganic materials: glass ceramics, sintering ceramics, cement, and geopolymers. Furthermore, their properties, chromium solidification ability, and mechanism are summarized. Based on these experimental data and theories, future research in the field will likely focus on the following aspects: (1) establishing a systematic database of inorganic materials used to treat CCSW, comprehensively considering their chromium solidification ability and maximum waste consumption; (2) saving energy, simplifying the processes, and generating products with high added value; and (3) investigating the long-term chromium-leaching behavior of inorganic materials in different environments in order to improve the safety evaluation of materials prepared from CCSW.

INTRODUCTION

Chromium-containing solid waste (CCSW) is an important industrial waste mainly produced during the manufacturing of metal chromium, chromium salt, chromium ferroalloy, stainless steel, and leather. As a major producer and consumer of chromium resources, China accounted for 40% of the world's chromium ore production in 2018 (Fig. 1), which is mainly used in the refractory and casting industry, metallurgy, and chemical industries (Fig. 2). A large number of CCSWs are produced every year in these fields, typically including metallurgical CCSWs such as slag/dust/pickling sludge produced in stainless-steel making; chromium slag produced in the production of metal chromium, chromium salt, and ferrochrome alloy; and various slags and muds produced by the leather industry. According to the statistics, each ton of stainless steel produces 18–33 kg of dust and approximately 250 kg of steel slag. In addition, rolled steel sheets and pickling sludge account for approximately 1–3% and 3–5% of stainless-steel output, respectively. China's annual output of stainless steel is close to 30 million tons, which generates nearly 10 million tons of CCSW every year. Chromite ore processing residue (COPR) is a byproduct of the chromite alkaline roasting process. The total amount of COPR in China is estimated to exceed 6 million tons, with an annual increase of nearly 60,000 tons every year.[3] In the field of leather manufacturing, one ton of wet leather can only produce 200 kg of finished leather, but it will produce more than 250 kg of chromium-containing leather waste. Data from 2016 shows that the global annual production of raw leather is about 694.53 million tons.[4,5] Therefore, the impact of CCSW cannot be ignored. In view of the potential leaching harm of chromium to the environment and society, stainless-steel pickling sludge has been clearly listed as hazardous solid waste. Comprehensive treatment of this type of solid waste is of particular importance. However, to date, this type of solid waste has not been fully or well utilized. Traditional treatment methods, such as stacking and burying, not only waste resources but also cause dust pollution and harm the environment. At the same time, leaching and oxidized Cr^{6+} has a carcinogenic

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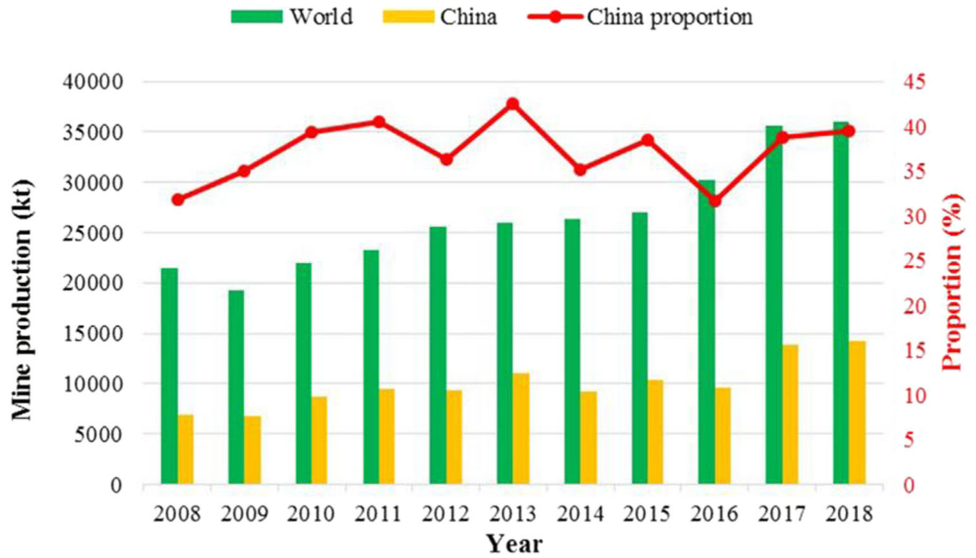

Fig. 1. Global and China chromite production in 2008–2018 (reprinted from Ref. [1]).

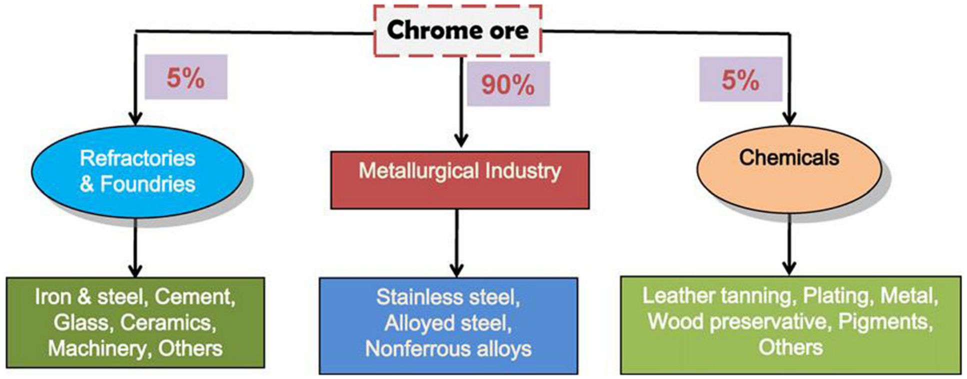

Fig. 2. Application field of chromite (reprinted from Ref. [2]).

effect on the human body. The main components of common chromium-containing solid wastes are shown in Table I.

Currently, the largest constituents of CCSW (slag, dust, and mud produced by the metallurgical industry) can be divided into the following three systems according to the data: (1) a low-chromium-containing silicate system of CaO-Al_2O_3-MgO-SiO_2-Cr_2O_3; (2) a high-chromium-containing system of Fe_2O_3-Cr_2O_3-Al_2O_3-MgO-SiO_2; and (3) a high-chromium-containing system of CaF_2-Fe_2O_3-Cr_2O_3. Among the solid wastes of the leather industry, CCSWs are mainly divided into sludge without C and tanned waste containing C, while the main component of COPR is based on MgO-Al_2O_3-Fe_2O_3-Cr_2O_3. Owing to the different production processes, the existing forms of chromium in CCSW are also different. Since the smelting process is usually carried out at a high temperature of 1500–1600°C, the chromium element in the metallurgical slag mainly exists in the form of spinel, whereas in other solid wastes such as pickling sludge, chromium tanned-leather waste, and sludge, CCSWs are derived from acid–base chemical reactions, in which a large amount of chromium exists in the form of CrO_4^{2-}. The data show that the proportion of hexavalent chromium in COPR accounts for 30%.[15] Therefore, the hazards of different types of CCSWs are different.

Nowadays, the main treatments of CCSW are mainly based on two routes: solidification/detoxification, and recycling. In terms of the former route, hexavalent chromium in CCSW is the main problem. The research mainly consists of biomass/reducing gas/chemical reagent reduction of hexavalent chromium in solid waste,[19–23] electrochemical removal of chromium from waste,[24] extraction of chromium by chemical leaching,[25,26] composite material solidification,[27] and vitrification solidification.[28] As for recycling, there has been research into obtaining chromium-containing raw materials by calcining leather industrial sludge as a substitute for chromium-containing ore.[17] Other researchers have prepared carbon nanofibers,[29] ceramic raw materials,[16] and aluminum based composites[30] from solid wastes of the leather

Table I. Chemical composition of chromium containing solid waste

	Chemical composition (wt%)						
Cr-bearing waste	**CaO**	**Al_2O_3**	**MgO**	**SiO_2**	**Fe_2O_3**	**Cr_2O_3**	**References**
Stainless steel EAF slag	39.8	9.7	7.2	33	0.9	2.8	6
	46.9	2.3	6.22	33.5	0.36	2.92	7
Stainless steel AOD slag	54.1	4.91	6.3	26.5	0.63	1.83	7
	58.4	2.1	2.1	26.4	-	0.3	8
Stainless steel EAF dust	14	0.7	2.6	5.6	45.2	14.3	9
	9	0.64	3.63	5.14	51.3	16.3	10
Ferrochromium slag	0.5	29.64	31.51	28.89	-	7.6	11
	6.13	23.21	20.86	29.14	4.01	12.59	12

	CaO	**SiO_2**	**CaF_2**	**$CaSO_4$**	**Fe_2O_3**	**Cr_2O_3**	
Pickling sludge	7.95	1.15	42.7	8.5	17.5	5.07	13
	-	9.3	45.71	-	25.52	5.01	14

	CaO	**MgO**	**Al_2O_3**	**SO_3**	**Cl**	**Cr_2O_3**	
Leather waste sludge	7.12	20.9	3.97	14.7	7.37	33.5	16
	18.45	4.56	4.55	7.71	25.52	45.01	5

	C	**N**	**O**	**H**	**S**	**Cr**	
Chromium-tanned leather waste	44-48	14-15	21-2	5.8-6.2	1.0-2.0	2.6-3.9	17

	SiO_2	**MgO**	**Al_2O_3**	**Na_2O**	**Fe_2O_3**	**Cr_2O_3**	
COPR	5.82	14.54	12.34	5.18	47.94	11.73	15
	1.18	12.62	20.9	-	41.87	14.76	18

industry. Yet other studies adopted chemical/biological technology to repair chromium polluted environments.[2,31] However, most of the treatments focused on CCSW with small total capacity, such as leather sludge and COPR. Owing to their high energy consumption, the above methods are very difficult to apply in industry, and are not in line with the concept of green sustainable development; therefore, they are not suitable for large-scale treatment of solid waste, especially metallurgical CCSW.

For metallurgical CCSWs with high chromium content, such as stainless-steel dust, it is common to extract valuable metals using fire reduction. Typical processes include the American Inmetco process[32] and FASTMET process,[33] the Star process used by Kawasaki in Japan, the Plasmdust process of the Swedish company SKF, IPBM (a plant byproduct melting process), and the OxyCup process.[34,35] The core principle of these processes is to reduce Cr/Fe/Ni and other elements into molten metal, which is combined with carbon and other reducing agents at high temperatures, and then the metal is separated from the residue. For Chinese enterprises, it is common to transfer stainless-steel dust to ferroalloy plants to produce Fe-Cr (–Ni) alloy in a submerged arc furnace or utilize the dust as a raw material in the stainless-steel production process, in which Fe/Cr/Ni and other elements are reduced and recovered. Through these processes, a high recovery ratio of Fe/Cr/Ni can be achieved, which motivates enterprises to deal with this type of CCSW. However, at the same time, secondary solid waste with residual chromium content is also produced. For solid wastes with low chromium content (less than 3%), such as argon oxygen decarburization (AOD) slag or secondary waste generated after reduction, metal recovery is difficult and inefficient. Therefore, a different method is needed for the detoxification and solidification of chromium.

Using CCSW to prepare inorganic materials can achieve resource utilization and the solidification/detoxification of CCSW simultaneously. Since CCSW is rich in reusable resources such as CaO, Al_2O_3, MgO, SiO_2, and Fe_2O_3, it is highly suitable for the preparation of inorganic materials such as glass ceramics, sintered ceramics, cement, and geopolymers when supplemented with a certain amount of modifier. On the one hand, solid waste replaces natural stone and clay resources to avoid damage to the environment caused by over-exploitation. On the other hand, turning waste into wealth and reducing further pollution to the environment caused by accumulation can bring great economic benefits to enterprises. More importantly, inorganic materials can effectively solidify harmful heavy-metal elements in the crystal structure to inhibit leaching into the environment. From the perspective of green sustainable development, the preparation of materials from solid waste has extensive and far-reaching significance. However, to date, the preparation of inorganic materials from CCSWs has not yet been popularized and applied on a large scale in China. The core problem is that the construction industry doubts the safety of the prepared products. At the same time, the impact of CCSW on the performance of different inorganic materials remains unclear.

Therefore, this paper reviews the current research status of preparing various inorganic materials from CCSW, summarizes the influence of chromium-containing raw materials on the properties of the prepared inorganic materials from the aspect of practicability, and evaluates the chromium stabilization ability and mechanism of inorganic materials from the aspect of safety. Finally, the existing problems in the application of inorganic materials prepared from CCSW are concluded, and this area is emphasized as a focus of future research. The aim of this study was to provide a comprehensive reference for the utilization of CCSWs.

GLASS CERAMICS

Research Status of Glass Ceramics Prepared from CCSW

Glass ceramics, which contain a large number of small mineral grains and residual glass, are inorganic materials prepared by controlling the crystallization of the appropriate glass. The glass is held at the glass transition temperature to promote nucleation and then at the crystallization exothermic temperature to facilitate crystallization. The main methods of preparation include: (1) the bulk crystallization method, (2) the sintering method, and (3) the sol-gel method.[36] Owing to the limitations of the process conditions, raw materials, and cost, the first two methods are usually applied to produce glass ceramics from solid waste.

To date, the theoretical laboratory research on the preparation of glass ceramics from CCSW, which includes municipal-solid-waste incineration ash, pickling sludge, stainless steel slag, chromium iron slag, and others (Table II), is relatively mature. Relevant studies have the following aspects in

Table II. Research on preparation of glass ceramics from CCSW

Solid waste	Cr content and addition amount of raw material	Preparation heat treatment	References
MSWI fly ash, pickling sludge and waste glass	22 wt.% pickling sludge	Melted at 1400 °C for 3 h, nucleated and crystallized at 800 °C for 0.5 h	39
Stainless steel slag	Stainless steel slag (1.82 wt.% Cr_2O_3)	Melted at 1450 °C for 3 h, and heated at the required temperatures	40
Fly ash and bottom ash	14 wt.% fly ash (0.03 wt.% Cr_2O_3) 74 wt.% bottom ash (0.12 wt.% Cr_2O_3)	Foamed at 1150 °C for 30 min	41
Stainless steel slag and pickling sludge	Stainless steel slag (<3.07 wt.% Cr_2O_3) Pickling sludge (< 9.49 wt.% Cr_2O_3)	Melted at 1460 °C for 1 h, and heated at the required temperatures (680–930°C)	42
Heavy metal gypsum and pickling sludge	Pickling sludge (4.55 wt.% Cr_2O_3)	Melted at 1460 °C for 2.5 h, nucleated at 700 °C for 2 h, and crystallized at 900 °C for 1h	43
Stainless steel slag	Containing: 0.55–1.27 wt.% Cr_2O_3	Melted at 1500 °C for 3 h, and heated at the required temperatures	44
AOD stainless steel slag	40–80 wt.% AOD slag (2.1 wt.% Cr_2O_3)	Melted at 1500 °C for 1 h, and heated at the required temperatures	45
Stainless steel slag and iron tailings	Containing: 0–1.2 wt.% Cr_2O_3	Melted, nucleated at 690 °C for 2 h, and crystallized at 880 °C for 2 h	46
High-carbon ferrochromium slag	30–50 wt.% slag (4.89 wt.% Cr_2O_3)	Melted at 1550 °C for 2 h, and heated at the required temperatures	47

common. (1) Most studies have adopted the bulk crystallization method. After crystallization, the exothermic temperature was determined from the differential scanning calorimetry curve, and the corresponding heat treatment process was carried out to obtain the glass ceramic products. The advantage of this method is that the chromium within CCSW can be evenly dispersed during the melting process to avoid the formation and enrichment of chromium-containing phases, which leads to leaching and safety problems. (2) Owing to the large amount of alkaline oxides (CaO and MgO) in CCSW, glass network formers, such as silicon-rich materials, need to be added to adjust the composition. Therefore, most of the glass ceramics prepared from CCSW were based on the CaO–MgO–Al_2O_3–SiO_2 system, in which the common main mineral phase was pyroxene. Yu Shi et al. showed that Cr_2O_3 can effectively refine the grain of diopside. At the same time, the orientated growth of diopside on magnesium chromium spinel was confirmed by the electron back scatter diffraction (EBSD) results,[37] which proved that the preparation of pyroxene-based glass ceramics from CCSW has an innate advantage. (3) Although the compositions of the treated CCSWs were different, the chromium content in the raw materials was in the range of 0.05–3 wt.% after adding pure reagent additives or other solid waste. Zhang et al. showed that when Cr_2O_3 in the melt exceeded 3 wt.%, the excessive formation of spinel had a negative impact on the mechanical properties of the material.[38] Therefore, the Cr_2O_3 content in the raw materials should be strictly controlled when preparing glass ceramics.

Physical and Chemical Properties of Glass Ceramics Prepared from CCSW

Table III shows the mineral phases and physical and chemical properties of the glass ceramics prepared from CCSW. Based on the aforementioned CaO–MgO–Al_2O_3–SiO_2 glass ceramics system, the mineral phases of the prepared materials mainly include diopside, wollastonite, akermanite, gehlenite, and spinel. Relevant studies on diopside, the most dominant phase, have shown that it has good mechanical properties and chemical corrosion resistance.[49] Therefore, the excellent characteristics of the mineral phase and the polymerization of a large number of fine grains have been fully combined to improve the performance of the glass ceramics.

In terms of mechanical properties, the glass ceramics prepared from CCSW possessed higher flexural strength and microhardness than those of natural stone, reaching 80–200 MPa and 5–10 GPa, respectively. Among glass ceramics, the flexural strengths of those prepared from stainless steel slag,[40] and AOD slag[45] reached 176 and 137 MPa, and the microhardness reached 5–10 GPa,[43] which is much higher than the strength of natural stone. Guo et al. found that Cr_2O_3 promoted the formation of diopside interleaving structures when synthesizing chromium-containing glass ceramics using pure reagents.[50] Zhang et al. found that Cr_2O_3 plays a

Table III. Mineral phases and physicochemical properties of glass ceramics prepared from CCSW

Material	Mineral phases	Properties	References
MSWI fly ash and pickling sludge-based glass ceramics	Diopside and spinel	Vickers hardness 13.11 GPa, flexural strength 135.84 MPa, acid and alkali resistances 98.65% and 99.88%	39
Stainless steel slag-based glass ceramics	Wollastonite-augite	Bending strength 176.21 MPa, Vickers hardness 8.81 GPa,	40
Fly ash and bottom ash-based foam glass ceramics	Gehlenite and akermanite	Porosity 76.03%, low bulk density 0.67 g/cm^3, compressive strength 10.56 MPa	41
Stainless steel slag and pickling sludge	Diopside, augite, and cuspidine	Flexural strength: 126.5 MPa, compressive strength 606 MPa, 0.04% water adsorption	42
Heavy metal gypsum and pickling sludge-based glass ceramics	Akermanite	Microhardness: 5.3 GPa, bending strength: 206 MPa, water absorption: 0.13%	43
AOD stainless steel slag	Diopside–akermanite–gehlenite	Highest flexural strength: 137.83 MPa, acid and alkali resistances: 99.919% and 99.991%, Mohs hardness:7	45
Picking sludge and waste glass	Calcium aluminum silicate and nepheline	Bending strength: 77 MPa, acid and alkali resistances: 99.9% and 98.7%	48

significant role in the grain refinement of magnesium-rich glass ceramics.[51] These results show that Cr_2O_3 in CCSW can effectively enhance the mechanical properties of glass ceramics. In terms of chemical corrosion resistance, the acid and alkali resistances of the materials were in the range of 97–99%. For example, the acid and alkali resistances of diopside glass ceramics prepared from sludge and fly ash reached 98.65% and 99.88%, respectively,[39] indicating good stability in various extreme environments. Based on these properties, CCSW-based glass ceramics have great application potential in constructing walls and pavements in the future.

In conclusion, glass ceramics have the capability to absorb CCSW with a high Si/Al content on a large scale, such as from stainless steel slag and ferrochromium slag. Moreover, glass ceramics can absorb other solid wastes, such as fly ash, waste incineration ash, and sludge. However, application of this route on a large scale is difficult because it is necessary to build a corresponding melting heat treatment production line, in which the melting temperature must reach 1400–1600°C, which greatly increases the cost. The results in "Research Status of Glass Ceramics Prepared from CCSW" section show that there are significant differences in the temperature and duration of heat treatment. In addition, considering the mechanical properties of the materials, although the strength of the prepared materials is higher than that of natural stone, excessive strength will increase the difficulty of machining. The preparation of glass ceramics from CCSW should be carried out in accordance with the principles of low cost and short processing times.

Therefore, future research should focus on the collaborative preparation of various solid wastes, improve the consumption amount of solid waste, add solid wastes with heat value to improve the melting efficiency, shorten the heat treatment time, and reduce the heat treatment temperature. Through these measures, the energy input in the preparation process would decrease, ultimately improving the industrial application feasibility of the route.

SINTERING CERAMICS

Research Status of Sintering Ceramics Prepared from CCSW

To prepare sintering ceramics from solid waste, raw materials are usually mixed with auxiliary materials such as feldspar, quartz, clay, or fly ash and fully ground, pressed, and sintered at a specific temperature to obtain products. This technical route has the following characteristics. (1) Owing to the composition of solid waste, which is abundant in $CaO/MgO/Al_2O_3/SiO_2$ and other substances and close to that of ceramic raw materials feldspar and clay, solid waste could be used to replace parts of raw materials. (2) The consumption of waste is extensive, and the added proportion can reach 40–60%. (3) Compared with the preparation process for glass ceramics, that for sintering ceramics is simpler, and target mineral phases are formed by a solid–solid reaction without a melting stage.

Table IV. Research on preparation of sintering ceramics from CCSW

Solid waste	Material	Cr content and addition amount of raw material	Preparation heat treatment	References
EAF steel slag	Ceramic tile	EAF slag (1.23wt.% Cr_2O_3)	Maximum firing temperature:1200 °C	55
Aluminum chromium slag	Colored zirconia ceramics	Add 0–15 wt.% Aluminum chromium slag	At 600 °C for 1h, then sintering at 1400/1500/1600 °C for 2 h	56
Ferrochromium slag	Porous cordierite ceramics	Ferrochromium slag (7.37 wt.% Cr_2O_3) Mixture (3.4 wt.% Cr_2O_3)	Sintered for 3 h from 1100 to 1400 °C	57
EAF Stainless steel slag	Black ceramic tiles	EAF slag (14.57 wt.% Cr_2O_3)	Sintered at 1150 °C for 30 min	58
Stainless steel slag	Ceramic body	Slag (2.66 wt.% Cr_2O_3) Ceramic body (1.71 wt.% Cr_2O_3)	Sintered at 1150 °C for 5 min	59
Ferrochromium slag	Ceramic brick	0–30 wt.% slag (5.17 wt.% Cr_2O_3)	Sintered at 900 °C for 2 h	60
Ferrochromium slag	Spinel-corundum ceramics	45–60 wt.% slag (6.09 wt.% Cr_2O_3)	Sintered at 1280–1360 °C	61
Chromium slag	Ceramic foam	5–60 wt.% (7.36 wt.% Cr_2O_3)	Heated at 1200°C for 60 min	62

Table V. Mineral Phases and Physicochemical Properties of Sintering Ceramics Prepared from CCSW

Material	Mineral phases	Properties	References
Aluminum chromium slag-based ceramics	ZrO_2, chromium corundum	Bending strength: 433.5 MPa (add 5.0 wt.% aluminum chromium slag)	56
Ferrochromium slag-based porous ceramics	Cordierite	Flexural strength 47.26 ± 1.01 MPa, CTE of 3.5 × 10^{-6}/°C^{-1}	57
EAF stainless steel slag-based ceramics	Diopside, $FeCr_2O_4$, $Cr_{1.3}Fe_{0.7}O_3$	Compressive strength: 8.23–58.12 Mpa	58
Stainless steel slag-based ceramic	Diopside, SiO_2	Collapsing strength: 3462.4 N Modulus of rupture: 57.3 Mpa	59
Ferrochromium slag-based ceramic brick	Quartz, hematite, spinel, forsterite	Mechanical strengths: > 7 MPa Thermal conductivity: decreases 42.3%	60
Ferrochromium slag-based ceramic	Spinel, corundum, sapphirine, indialite	5.08% Breakage ratio under 52 MPa Apparent density: 3.03 g/cm^3	61
Chromium slag-based ceramic foam	Quartz, spinel, magnesium aluminum chromium oxide	Bulk density: 0.191 g/cm^3, superior compressive strength:1.3 MPa, pore size: 0.73mm	62

In recent years, scholars have mainly focused on the preparation of sintering ceramics from blast furnace slag and steel slag. This is mainly because the composition of these slags resembles the CaO-MgO-Al_2O_3-SiO_2 system, which is more conducive to reducing the addition of auxiliary materials.[52–54] From CCSW, ceramic tiles, porous ceramics, foam ceramics, and spinel corundum ceramics were prepared using the sintering method (Table IV). Among these ceramics, the most representative are porous cordierite ceramics prepared from ferrochrome slag,[57] black ceramic brick prepared from electrical arc furnace (EAF) slag,[58] and spinel corundum ceramics prepared from ferrochrome slag.[61] These studies reported the following advantages of preparing sintering ceramics from CCSW: (1) a large amount of solid waste with a relatively high chromium content could be utilized; (2) the firing temperature is generally in the range of 1000–1200°C, which is convenient for practical applications; and (3) various types of ceramics with a wide range of applications can be prepared.

Physical and Chemical Properties of Sintering Ceramics Prepared from CCSW

Table V shows the mineral phases and properties of the sintering ceramics prepared from CCSW. It can be seen that the research paid more attention to physical properties than chemical. According to the application field of ceramics, these studies can be divided into three categories. The first category is building ceramics, which possess excellent mechanical properties (mineral phases: Cr_2O_3, spinel, and pyroxene). In particular, the compressive strength of ceramics prepared by EAF slag can reach 58.12 MPa.[59] The second category is functional ceramics such as cordierite ceramics, which have good thermal stability. The thermal expansion coefficient of cordierite ceramics prepared from chromium iron slag is 3.5 × 10^{-6}°C^{-1}, much lower than that of metal (Al: 23.3 × 10^{-6}°C^{-1}; Fe: 12.2 × 10^{-6}°C^{-1}). Structural ceramics, such as the foam ceramics of spinel and Mg/Al/Cr oxides, comprise the third category. The overall density of porous ceramics prepared from chromium slag is only 0.191 g cm^{-3}, and the pore diameter is 0.73 mm, which is suitable for use as a sound-absorbing material.[62] These ceramics have excellent properties and meet various standards for their applications. However, it is noteworthy that the effect of Cr_2O_3 on the material properties is not always positive. For example, when more than 5 wt.% slag was added to ZrO_2-based ceramics prepared from aluminum chromium slag, the mechanical strength of the material decreased significantly.[56] In addition, research has also shown that in the cordierite MgO–Al_2O_3–SiO_2 system, excessive Cr_2O_3 formed a spinel phase. Owing to the difference in strength between spinel and cordierite, the overall mechanical strength of the material was reduced.[63] Therefore, it is necessary to consider the formation of spinel when using CCSW to prepare sintering ceramics.

In summary, the preparation of sintered ceramics from CCSW is relatively simple in terms of the process, requires low energy and material investment, and is more amenable to industrial applications. However, the core problem is that the consumption of solid waste is relatively limited, which is attributed to the composition of the CCSW.

Generally, sintered ceramics should be prepared from Si/Al raw materials, while pickling sludge and CCSW from the leather industry are obviously unsuitable for a large amount of utilization. In addition, owing to the low-temperature solid–solid reaction during heat treatment, the toxic hexavalent chromium in CCSW cannot be detoxified without a reducing agent, and the prepared products still pose great risk. At the same time, determining how adding chromium-containing raw materials affects the properties of the prepared materials is still in the exploratory stage. In many of the aforementioned studies, CCSW has a negative effect on the properties of the prepared materials. Therefore, it is necessary to evaluate the type and dosage of CCSW for sintered ceramics preparation.

CEMENT

As a typical gel material, cement can solidify gravel firmly together after mixing with water, stirring into paste, and hardening. This material has been widely used in the construction industry owing to its excellent mechanical strength and corrosion resistance. Until now, relevant studies have used solid wastes such as waste glass, metal-containing chemically precipitated sludge,[64] and red mud[65] to prepare cement clinker. In addition, according to the statistics, the world and Europe produce nearly 50 and 12 million tons of steel slag, respectively, every year. Approximately 65% of slag is used in the construction field, and approximately 37% is used in cement production, which shows that the preparation of cement from solid waste has great application prospects.[66] However, owing to the complex composition of CCSW and the existence of free calcium oxide, research on the preparation of cement from CCSW has been relatively limited. In recent years, researchers have focused on the various forms of chromium in cement and its impact on cement performance to simulate actual CCSW. Generally, chromium doping methods include adding Cr_2O_3 to the cement clinker material and adding Cr^{3+}/Cr^{6+} to the aqueous solution.

Existing form of Cr_2O_3 in Cement and Its Impact on Cement Properties

Sinyoung et al. added 0.1–5 wt.% Cr_2O_3 to cement clinker raw material. The cement product was obtained after calcination at 1450°C for 90 min,[67] and the results showed that the main chromium-containing phases in cement clinker were $Ca_6Al_4Cr_2O_{15}$, $Ca_5Cr_3O_{12}$, $Ca_5Cr_2SiO_{12}$, and $CaCr_2O_7$. Li et al.[68] also observed the formation of a high-valence chromium phase, $Ca_4Al_6CrO_{16}$, while researching the preparation of tricalcium silicate cement clinker mixed with Cr_2O_3. These results indicate that the reaction of lime and other substances with Cr_2O_3 produces a high-valence chromium phase during roasting. Subsequently, Sinyoung et al. mixed the synthetic clinker with water in a water/cement ratio of 0.45. During hydration, $Ca_5(CrO_4)_3OH$, $CaCrO_4{\cdot}2H_2O$, $Al_2(OH)_4CrO_4$, and other hydrated phases appeared in the cement samples, which affected the relative contents of the $Ca(OH)_2$ and C–S–H gel. Stephan et al. found that the excessive addition of Cr_2O_3 leads to an increase in free calcium oxide and the decomposition of tricalcium silicate.[69] As for the cement properties, the results showed that the addition of Cr_2O_3 reduced the hydration exothermic temperature, and the exothermic peak gradually decreased. The initial and final setting times of the cement increased from 50 and 78 min for the reference sample to 980 and 1189 min, respectively. The compressive strength at 7 and 28 days also decreased from 18.2 and 29.2 MPa to 5.6 and 11.2 MPa, respectively.[67]

Existing form of Cr^{3+} Ion in Cement and Its Impact on Cement Properties

Niu et al.[70] used a $Cr(NO_3)_3{\cdot}9H_2O$ solution mixed with cement clinker to study the stabilization effect of sulfoaluminate cement and ordinary Portland cement on heavy metals. The results showed that when Cr^{3+} ions were doped into sulfoaluminate cement mortar, a new type of bentonite, $Ca_6Cr_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$, was formed, which indicated that Cr^{3+} ions replace Al^{3+} ions in ettringite to form bentonite.[71] In terms of material properties, the addition of Cr^{3+} ions increased the initial and final setting times and decreased the flexural strength. In contrast, the Cr^{3+} ion had relatively little effect on Portland cement, and the crystal phase did not change significantly. However, the diffraction peak intensity of calcium hydroxide after 28 days was reduced. In terms of properties, the Cr^{3+} ion had little effect on the setting time and flexural strength.

Zong et al.[72] solidified Cr^{3+} ions using magnesium sulfate cement. They found that after hydration, chromium mainly exists in two phases, $Cr(OH)_3{\cdot}3H_2O$ and $4Cr(OH)_3{\cdot}Cr_2H_2(SO_4)_4{\cdot}2H_2O$, and some Cr^{3+} ions replaced Mg^{2+} ions. As for material properties, the Cr^{3+} ions inhibited hydration and reduced the mechanical strength of the cement. However, the compressive strength of the solidified body at 28 days was 27.6 MPa, which was still much higher than the compressive strength required for hazardous waste landfill materials.

Lu et al.[73] studied the stabilization effect of tricalcium silicate on Cr^{3+} ions and obtained different results. They believed that the addition of 0.5% and 1% Cr^{3+} ions accelerated the hydration process, while adding more than 1.5% Cr^{3+} ions significantly delayed the hydration process. In addition, Cr^{3+} ions inhibited the formation of C–S–H and the polymerization of the silica tetrahedron. In particular, the chromium-rich phase $CaCrO_4{\cdot}H_2O$ appeared upon adding 3% Cr^{3+}.

Existing form of Cr^{6+} in Cement and Its Impact on Cement Properties

Jain et al.[74] used potassium dichromate solution as a doping agent for Cr^{6+} to investigate the hydration properties of marble powder–Portland cement mixed-gel material. In the field of mineral phases, the results showed that the samples after hydration were composed of calcium hydroxide, tricalcium silicate, dicalcium silicate, ettringite, bentonite, and two chromium-containing phases: chromium-containing ettringite and calcium chromate. The addition of Cr^{6+} ions increased the initial and final setting times, and the flexural strength of the cement decreased inversely. In addition, the authors also believed that the addition of marble powder weakened the negative effect of Cr^{6+} ions, which may be due to the formation of chromium-bearing bentonite. Trezza et al.[75] obtained similar conclusions when studying the effect of Cr^{6+} ions on the cement hydration process. Their study indicated that the existence of Cr^{6+} ions hindered the early hydration reaction of Portland cement.

While researching the effect of calcium sulfate on Portland cement for solidifying Cr^{6+} ions, Zhang et al.[76] reached a similar conclusion to that of Jain et al. They observed that Cr^{6+} ions increased the initial and final setting times, and the compressive strength of the calcium sulfate–chromium(VI) clinker paste was always lower than that of the calcium sulfate clinker paste. In addition, the authors also believed that the Cr^{6+} ions formed a CrO_4-U phase similar to the SO_4-U phase ($3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}0.5Na_2SO_4{\cdot}15H_2O$).

Osamu Yamaguchi et al.[77] found that 50–80% of the chromium extracted from Portland cement was Cr^{6+} ions. More importantly, chromium was more enriched in the calcium–aluminum–iron phase than in the calcium–silicon phase in the cement. Ivanov et al.[78] found that the addition of Cr^{6+} ions consumed a large amount of calcium aluminate, delayed the hydration reaction, and significantly reduced the compressive strength after 7 days. However, owing to the large amount of boehmite, the compressive strength was less affected by Cr^{6+} ions in the later stages of hydration. Zhang et al.[79] reached a similar conclusion for Cr^{6+} stabilization in calcium aluminate cement. The addition of Cr^{6+} inhibited the formation of the hydration products CAH_{10} and C_2AH_8, and thus the main hydration products were AH_3, CrO_4-C_3AH_6, and CrO_4-U.

In summary, the aforementioned research shows that there are safety issues with the preparation of cement clinker from CCSW, and the transformation of the chromium valence state is difficult to control during the roasting process. Therefore, future research should continue to eliminate CCSW based on the principle of solidification and adopt different types of cement for solidification according to the characteristics of the CCSW. In addition, the curing ability of cement for chromium ions is quite different depending on the chromium valence state, so it is necessary to have a clearer understanding of the valence proportion of chromium in CCSW. At the same time, the study should also consider the pretreatment of CCSW (e.g., physical crushing, chemical reagent treatment, vitrification, addition of reducing agent) to reduce the safety risk of its use.

GEOPOLYMERS

Geopolymers are three-dimensional (3D) polymers composed of $[SiO_4]^{4-}$ and $[AlO_4]^{-}$ tetrahedra. After activating the powder using an alkaline activator, the polymer product is obtained. Owing to its excellent performance and lower amount of CO_2 emitted during its preparation compared to that of cement, geopolymers have the potential to replace Portland cement. At present, the main methods of preparing geopolymers from solid waste include: (1) mixing silicon- and aluminum-rich materials (such as fly ash) with solid waste, (2) alkaline activation, and (3) curing and setting. At present, studies exist on the preparation of solid-waste base geopolymers from blast furnace slag,[80] red mud,[81,82] zinc slag,[83] etc., but similar to the research on cement, few studies have actually investigated the addition of CCSW to the raw materials of geopolymers.

Existing form of Cr_2O_3 in Geopolymers and Its Impact on Geopolymer Properties

Guo et al.[84] studied the stabilization behavior of Cr_2O_3/Cr in fly-ash-based geopolymers and found that Cr_2O_3/Cr mainly existed in the form of a physical package in the geopolymer; no other chromium-containing phase was formed. Meanwhile, the addition of Cr_2O_3/Cr reduced the total porosity of the geopolymer and improved the compressive strength of the material. Panigrahi et al.[85] directly prepared geopolymers from high-carbon ferrochromium slag. Their research showed that the glass phase appeared in the geopolymer matrix after activation, and the chromium partially migrated into the glass phase. After hydration, the rod-like crystal microstructure was formed.

Huang et al.[86] reduced/solidified chromium-ore processing residue using a composite geopolymer combined with zero-valent iron. It was found that ettringite was formed in the geopolymer with the addition of chromium slag, and there was no chromium-containing phase in the matrix, indicating that chromium was mostly combined with amorphous products. In terms of material properties, owing to its inactive character, the addition of chromium slag led to a decrease in the compressive strength. In contrast, reduced chromium slag increased the content of sulfate ions in the matrix and formed more ettringite phase, which improved the mechanical strength of the geopolymer. Sun et al.[87] solidified chromium-ore processing residue with a kaolinite-based geopolymer. Their results showed that the $CaCrO_4$ phase in the residue was fully dispersed in the geopolymer matrix after curing. The S^{2-} anions promoted the reduction of Cr^{6+} ions to Cr^{3+} ions. In terms of properties, it was considered that doping with an appropriate amount of Cr^{6+} ions would strengthen the mechanical properties of the material, which differed from the research results of Huang et al.

Existing form of Cr^{3+} Ion in Geopolymers and Its Impact on Geopolymer Properties

Giorgetti et al.[88] found that Cr^{3+} ions existed as octahedrons in geopolymers and formed a Cr–O–Al bridge in a 3D silicon–aluminum network. Wang et al.[89] reported that the addition of Cr^{3+} ions led to a decrease in the diffraction peaks in the geopolymer, indicating that crystalline phases were more transformed into the amorphous phase. Fansuri et al.[90] studied the solidification of Cr^{3+} ions in Pt. Ipmomi fly ash. They found that the addition of excess Cr^{3+} ions increased the viscosity of the alkaline activator, which led to a reduction of ion mobility, a shortening of setting time, and the formation of $Cr(OH)_3$ in the matrix. The authors also assumed that an appropriate amount of Cr^{3+} ions would strengthen the mechanical properties of the material. The compressive strength reached 47.83 MPa, while the doping of excess Cr^{3+} ions reduced the compressive strength to 4.39 MPa. Guo et al.[84] also observed a similar phenomenon. Their study found that Cr^{3+} ions replaced Ca^{2+} ions in N–A–S–H and C–S–H gels, and the displaced Ca^{2+} ions reacted with $[SiO_4]^{4-}$ and OH^- to generate $Ca_5(SiO_4)_2(OH)_2$. When 0.5% Cr^{3+} ions were added, the total porosity of the geopolymer was less than that of the blank sample, and the compressive strength was improved. When the chromium content continued to increase, the compressive strength decreased significantly.

Chen et al.[91] studied the stabilization effect of a metakaolin-based geopolymer on ferrous chloride added to Cr^{6+} ions and found that the addition of ferrous chloride promoted the reduction of Cr^{6+} ions to Cr^{3+} ions, and Cr^{3+} ions did not form a chromium-containing phase. In terms of properties, with the gradual increase in ferrous chloride content, the compressive strength of the sample first increased and then decreased, which may be related to the increase in Cr^{3+} ions in the geopolymer.

Existing form of Cr^{6+} Ion in Geopolymers and Its Impact on Geopolymer Properties

Nikoli et al.[92] solidified Cr^{6+} ions using a fly-ash-based geopolymer. Their results showed that K_2CrO_4 crystallized and appeared in the matrix after high-temperature drying. The NMR data indicated that the addition of Cr^{6+} decreased the fraction of the aluminum-rich group Q4 (mAl), which led to a decrease in the compressive strength. Zhang et al.[93] also studied the stabilization effect of a fly-ash-based geopolymer on Cr^{6+} ions and found that the Cr^{6+} ions did not form chromium-containing phases in the matrix. The Fourier-transform infrared spectroscopy (FTIR) and energy-dispersive x-ray spectroscopy data showed that chromium was uniformly combined with the geopolymer. In terms of mechanical properties, the addition of Cr^{6+} ions decreased the compressive strength of the geopolymer at 7 and 14 days while improving the properties at 28 days. Abdullah et al.[94] also believed that Cr^{6+} ions were embedded into the network in the form of $CrO_4{}^{2-}$ ions and would not form a chromium-containing phase. Simultaneously, the addition of Cr^{6+} ions slowed the formation of the geopolymer.

In contrast to the research of Zhang et al., Ji et al.[95] prepared geopolymers from drinking water treatment residue (DWTR) and granular blast-furnace slag (GBFS). In addition to the calcite phase, the chromite $Fe(Cr,Al)_2O_4$ phase formed by Cr^{6+} ions also existed in the matrix. The FTIR data showed that the addition of Cr^{6+} ions led to the breaking of Si–O–Al bonds.

In summary, cement and geopolymer materials are vastly different in terms of their ability to stabilize chromium with different valence states. The addition of chromium-containing raw materials deteriorates the related properties. However, high Si/Al content industrial wastes such as fly ash and red mud can be utilized as the main raw material of geopolymers, which greatly reduces the cost and achieves the goal of collaborative treatment of solid wastes. At the same time, the alkaline excitation reaction has a significant impact on the mechanical properties and curing ability of geopolymers. Therefore, future research should determine an appropriate alkaline excitation reaction (i.e., type of excitation agent, reaction temperature, and time). In addition, the CCSW pretreatment process should be considered.

CHROMIUM LEACHING CHARACTERISTICS AND STABILIZATION MECHANISM OF INORGANIC MATERIALS

Chromium Leaching Characteristics of Inorganic Materials

To improve the safety of inorganic materials, the leaching characteristics of heavy metal chromium need to be evaluated. The evaluation results for typical chromium-containing inorganic materials are listed in Table VI. The results showed that the commonly used leaching standards are the toxicity characteristic leaching procedure (TCLP), the leaching toxicity horizontal vibration method (HJ 557-2010), etc. These leaching standards have the following commonalities: (1) accelerating the leaching reaction by vibration, centrifugation, etc.; (2) the leaching experiment is carried out for approximately 24 h, which is a short-term leaching process; (3) the leaching environment is generally neutral,

Table VI. Leaching standard and characteristics of chromium-containing inorganic materials

Material	Cr leaching standard and limitation	Cr leaching amount	References
MSWI fly ash and pickling sludge-based glass ceramics	Toxicity characteristic leaching procedure (TCLP) method: 5.0 mg/l	0.20 mg/l	39
Fly ash and bottom ash-based foam glass ceramics	Toxicity characteristic leaching procedure (TCLP) method: 5.0 mg/l	0.08 mg/l	41
Heavy metal gypsum and pickling sludge-based glass ceramics	Toxicity characteristic leaching procedure (TCLP) method: 5.0 mg/l	0.317 mg/l	43
AOD stainless steel slag-based glass ceramics	Leaching toxicity horizontal vibration method (HJ 557-2010): 1.5 mg/l	0.138 mg/l	45
EAF steel slag (ceramic tile raw material)	EN 12457-1:20002 (European Standard): 0.05 mg/l	0.005 mg/l	48
Ferrochromium slag-based porous ceramics	US EPA limits: 100 mg/kg	<35.0 mg/kg	60
EAF stainless steel slag-based ceramics	GB 5085.3-2007:15 mg/l	2.35 mg/l	61
Stainless steel slag-based ceramic	GB/T4100-2006:100 mg/kg	25.17 mg/kg	62
Cr_2O_3-added cement	Toxicity characteristic leaching procedure (TCLP) method: 5.0 mg/l	Total Cr: 26.9 mg/l Cr^{6+}: 24.39 mg/l (5 wt.% Cr_2O_3)	67
Cr^{3+} added basic magnesium sulfate cement	Leaching toxicity horizontal vibration method (HJ 557-2010):15 mg/l	0–0.25 mg/l	72
Cr^{6+} added marble dust blended cement	Toxicity characteristic leaching procedure (TCLP) method: 5.0 mg/l	Far more than the limitation: 50–450 mg/l	74
Cr^{6+} added Portland cement paste	Toxicity characteristic leaching procedure (TCLP) method: 5.0 mg/l	Far more than the limitation: 80–140 mg/l (2 wt.% Cr^{6+} added)	76
Cr^{6+} added calcium aluminate cement	Brazilian standard NBR 10005	1.9–7.7 mg/l (0.5–2.5% Cr added)	78
Cr^{6+} added calcium aluminate cement	Toxicity characteristic leaching procedure (TCLP) method: 5.0 mg/l	After curing 90 days: <5 mg/l (1% Cr added)	79
Cr^{3+} added fly ash-based geopolymer	Leaching toxicity horizontal vibration method (HJ 557-2010): 15 mg/l	0.07 mg/l (1% Cr added) 1.93 mg/l (3% Cr added)	84
Chromite ore processing residue based geopolymer coupled with zero-valent iron	Toxicity characteristic leaching procedure (TCLP) method: 5.0 mg/l	0.64–4.82 mg/l	86
Chromite ore processing residue added Metakaolin-based geopolymer	Toxicity characteristic leaching procedure (TCLP) method: 5.0 mg/l	more than 45 mg/l (mole: $S^{2-}/Cr(VI) = 0$) 1.37 mg/l (mole: $S^{2-}/Cr(VI) = 10$)	87
Cr^{6+} added metakaolin-based geopolymer coupled with ferrous chloride	Toxicity characteristic leaching procedure (TCLP) method: 5.0 mg/l	0.42 mg/l (1.5 wt.% $FeCl_2 \cdot 4H_2O$ added) 20.05 mg/l (0.5 wt.% $FeCl_2 \cdot 4H_2O$ added)	91
Cr^{6+} added fly ash-based geopolymers	SRPS EN 12457-2:50 mg/kg (unsuitable for landfill)	12000–16000 mg/kg	92

such as pure water; and (4) the leaching behavior is evaluated based on the total chromium content in the leachate. However, Karayannis et al.[96] believed that the potential of heavy metals to migrate to the liquid phase mainly depends on the leaching method, type of leaching solution, and pH. Therefore, chromium leaching of materials in complex liquid environments still requires further research.

Moreover, it can be seen that the chromium leaching amount of chromium-containing glass ceramics and sintering ceramics was far lower than the national standard, while that of some cements and geopolymers was much higher than the standard. This phenomenon indicates that there are potential safety problems associated with the use of chromium-containing cement and geopolymer, which was closely related to the chromium stabilization mechanism.

Stabilization Mechanism of Chromium-Containing Inorganic Materials

According to current research, the stabilization mechanism of chromium-containing inorganic materials can be divided into three types. The first is to seal CCSW by physical wrapping, which has the potential risk of direct contact between CCSWs and the environment without the formation of chemical bonds. The second is to form a stable chromium-containing phase and solidify chromium into the mineral crystal structure. The solidification efficiency of this method is closely related to the crystalline phase. The third is gel solidification of the amorphous phase produced by the cement and geopolymer. Chromium ions are effectively solidified in the network structure of silicate and aluminosilicate, which includes the adsorption and substitution effects of ions. Relevant scholars have conducted research on these three stabilization mechanisms.

Physical Wrapping, Mineral Phase, and Structural Solidification

Liu et al.[97] found that when adding Cr_2O_3 into a CaO-Al_2O_3-SiO_2 glass ceramic system, the stabilization mechanism of chromium was physical wrapping. Most of the chromium content (82%) was embedded in the glass matrix as Cr_2O_3 crystals, and no other chromium-containing phases were generated. The remaining chromium content dissolved into the matrix network. However, after heat treatment, a certain amount of chromium-containing phase ($CaCrO_4$) was formed on the surface of the glass ceramics. Some studies have shown that this phase leads to a large amount of chromium leaching.[98]

Subsequently, scholars focused more on chromium-containing phases with excellent stabilization performance and considered promoting effective enrichment of chromium in these phases when preparing materials. Some studies have suggested that $MgCr_2O_4$ spinel can stably solidify chromium in the structure.[99,100] Based on this, many scholars have focused on the formation and growth of the spinel phase in glass ceramics and sintering ceramics, as well as the enrichment of chromium in spinel. Zhao et al.[101] used municipal-solid-waste incineration ash and pickling sludge to prepare glass ceramics. The results showed that the nature of the chromium changed from an oxidizable state to a residual state during heat treatment, which proved that the stability of heavy metals was greatly improved. Transmission electron microscopy and electron probe micro analyzer (EPMA) data confirmed that chromium existed in the spinel structure in the form of a solid solution. Song et al.[102] found that by reducing the crystallization temperature, the formation of spinel was promoted while inhibiting the generation of the main crystalline phase, $CaNiSi_2O_6$. Meanwhile, most of the Cr and Ni content was enriched and solidified in the spinel phase (Fig. 3).

When preparing CaO-MgO-SiO_2-Al_2O_3-Cr_2O_3-based glass ceramics, Liao et al.[103] found that during the preparation process, Cr(III), which was in a stable state above 1100°C in the raw material, was not oxidized to Cr(VI). With an increase in the Cr_2O_3 content in the system, the proportion of the spinel phase increased. The enrichment ratio of 2 wt.% Cr_2O_3 in the spinel phase was approximately

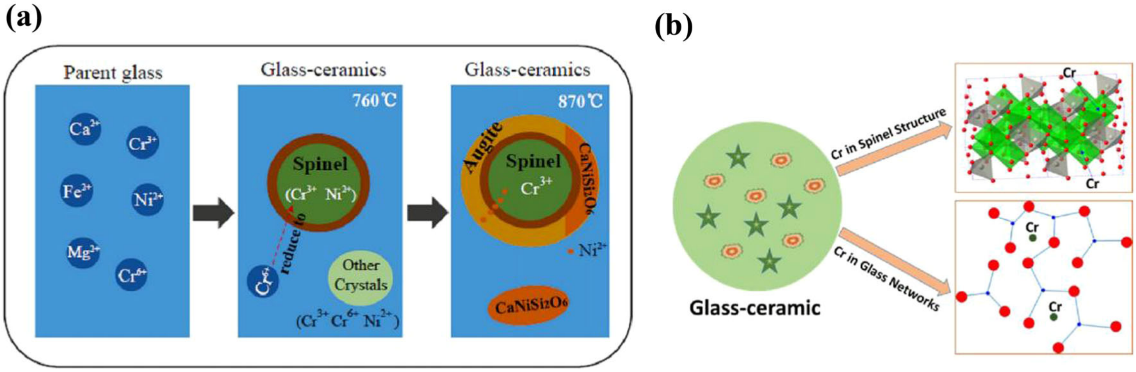

Fig. 3. Stabilization mechanism of chromium in spinel-containing glass ceramics. Reprinted from references (a) [102] and (b) [103].

70%, while it increased to 90% using 10 wt.% Cr_2O_3. An appropriate amount of Cr_2O_3 improved the enrichment ratio of chromium in spinel. Based on this study, Liao et al.[97] prepared glass ceramics from chromium-ore treatment residue and successfully detoxified Cr(VI) from raw material to Cr(III), which indicated that melting and heat-treatment processes can effectively reduce the harm of hexavalent chromium in CCSW.

In terms of adding other components to promote the enrichment of chromium in spinel, Wang et al.[104] found that excessive addition of Al_2O_3 caused Al^{3+} ions to replace Cr^{3+} ions in the spinel phase, thus reducing the enrichment ratio of chromium. Li et al.[105] mixed electroplating sludge with SiO_2, Al_2O_3, and Fe_2O_3 for sintering to study the solidification behavior of heavy metals in order to provide theoretical guidance for the production of clay bricks or ceramics from solid wastes containing heavy metals. It was found that the existence of CaO seriously affected the formation of chromium-containing spinel phase, and Cr(III) was oxidized to Cr(VI), which resulted in the leaching of chromium. These results proved that during the preparation of cement clinker, the chromium-containing phase generated by roasting chromium-containing substances and raw materials (such as lime) cannot be regarded as an effective phase for chromium stabilization. The high-valence-chromium-containing phases had strong leaching properties. Therefore, mineral phase solidification is not a suitable method for the direct preparation of cement clinker from CCSW.

Gel Solidification

In the preparation of cement, Belebchouche et al.[106] used Portland cement and CCSW to prepare materials. They found that CrO_5^{4-} ions can replace SiO_4^{4-} ions in the C–S–H gel and then produce the complex hydrated product $3CaO{\cdot}Cr_2O_3{\cdot}CaSO_3{\cdot}11H_2O$. Zhang et al.[79] also found a substitution phenomenon of Cr^{6+} ions in cement. It was shown that Cr^{6+} ions replaced sulfate in SO_4-U and tetrahedral hydroxyl in C_3AH_6 to form two hydration products that solidified chromium.

As for the preparation of geopolymers, Chen et al.[91] believed that during the process of preparing a chromium-containing geopolymer, negatively charged $[AlO_4]^-$ was first formed by geopolymerization. Meanwhile, the addition of Fe^{2+} ions reduced the Cr^{6+} ions to Cr^{3+} ions. Subsequently, Cr^{3+} was attracted by $[AlO_4]^-$ owing to electrostatic attraction and solidified in the geopolymer matrix. Wei et al.[107] concluded that the stabilization mechanism of chromium in fly-ash–kaolin geopolymer proceeded as follows: (1) adsorption—Al^{3+} ions formed tetrahedron $[AlO_4]^{5-}$ in an alkaline environment and then adsorbed Cr^{3+} ions to form the amorphous structure of the geopolymer; (2) generation of chemical bonds after polycondensation—Cr^{3+} ions polycondensated with amorphous aluminosilicate molecules of the geopolymer skeleton structure to form a single Si–O–Al(Cr) or double Si–O–Al(Cr)–O–Si silicon–aluminum network structure, which can further polycondensate by activating the alkaline environment. These network structures can form C–S–H gels and N/K–A–S–H gels with Ca^{2+} and Na^+/K^+. Xia et al.[108] also found that chromium ions in geopolymers were stabilized by two types of mechanisms: physical and chemical. Chromium ions replaced the charge-balance ions Ca^{2+} and Na^+ in the gel. Then, owing to the formation of chemical bonds, chromium ions were solidified in the amorphous phase.

In conclusion, in terms of chromium leaching evaluation, the inorganic materials prepared from CCSW are still evaluated according to the standards for solid wastes, but there are currently no corresponding standards to evaluate the safety of the prepared materials. Therefore, it is urgent to formulate these corresponding standards (such as the determination of chromium-leaching toxicity of glass ceramics, sintered ceramics, and other materials prepared from CCSW). In terms of the curing mechanism, the current research shows that the best curing form of chromium is the chromium-containing spinel phase. Therefore, it is suitable to enrich chromium in the spinel phase. However, chromium ions can be solidified in other crystalline phases and form chemical bonds with the gel structure; although they also have stabilization ability, there is still a risk during long-term leaching. Therefore, subsequent studies should focus on the long-term safety of these solidified forms and ensure that the materials are stable over a long period of time.

CONCLUSION AND FUTURE RESEARCH

The preparation of inorganic materials to consume chromium-containing solid waste (CCSW) is an environmentally friendly and value-added method. In recent times, scholars have mainly researched four types of materials: glass ceramics, sintering ceramics, cement, and geopolymers. Three conclusions can be deduced from the data. (1) In terms of performance, glass ceramics and sintering ceramics prepared from CCSW had good physical and chemical properties, while cement and geopolymers with chromium-containing substances still met the required standards of building materials, although their mechanical properties weakened. (2) Regarding the chromium solidification ability, the chromium leaching level of most glass ceramics and sintering ceramics prepared from CCSW was far lower than the national leaching standard, while the stabilization ability of cement and geopolymers for different valence states of chromium was quite different. Therefore, the valence of chromium in raw materials must be strictly controlled. (3) Concerning the stabilization mechanism, glass ceramics and sintering ceramics mainly stabilize chromium by mineral phases and structures, such as the formation of stable magnesium–chromium spinel and physical wrapping of the glass phase. By contrast, the chromium content in cement and geopolymers is mainly stored in the network structure of the gel by adsorption and ion substitution.

So far, although basic data have been obtained on the preparation of inorganic materials from CCSW, there is a certain distance from large-scale practical industrial applications, and the following aspects still require further study:

First, the characteristics of CCSW should be further evaluated in order to select the proper material preparation process. For example, according to the presented research, there were significant differences in the stabilization ability of cement and geopolymers for trivalent chromium and hexavalent chromium. Based on using the total chromium content in solid waste to evaluate its safety and availability, there may be potential leaching hazards during the preparation process. Therefore, it is necessary to establish a systematic large database of CCSW (including mineral phase and composition, existing form of chromium-containing phase, valence ratio of chromium element, etc.) and then comprehensively consider the chromium solidification ability of different inorganic materials, maximum consumption of solid waste, and on-site process conditions to select the appropriate technical route. In addition, based on the combination of two technical routes (i.e., material preparation and solid waste detoxification), detoxified CCSW (roasting modification, vitrification modification, chemical reduction, etc.) can be used as a raw material to prepare inorganic materials to further improve the safety of resource utilization.

Second, the preparation route must be optimized. In theory, CCSW is suitable for the preparation of glass ceramics. However, owing to the long heating treatment and high consumption, the technical route is difficult to implement on an industrial scale. Therefore, it is necessary to shorten the process and design a composition that can be used for the preparation of glass ceramics using a one-step method. In addition, owing to the excellent stabilization characteristics of glass ceramics, combining CCSW with other solid wastes to produce materials would significantly expand the application field. In contrast, the preparation process of sintering ceramics from CCSW is relatively simple, but the effect of chromium on the material properties remains unclear. Therefore, the development of sintering ceramics from CCSWs with high added value is a future research topic. In terms of cement and geopolymers, based on the current research, excessive doping of chromium has a negative effect on various material properties. More importantly, the chromium leaching amount significantly exceeds the standard. Therefore, it is necessary to systematically master the stabilization mechanism and corresponding leaching characteristics of the cement and geopolymer.

Finally, in terms of safety evaluation, most of the recent research used short-term evaluation standards of solid waste to determine the chromium leaching level of materials. However, chromium leaching is a long and continuous process. Therefore, the long-term chromium leaching behavior of inorganic materials in different environments (pH and leaching agent) should be further investigated to establish the corresponding leaching kinetic model. The fundamental data presented here can serve to improve the safety evaluation of inorganic materials derived from CCSWs.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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