

# Study on the Immobilisation Mechanism of Chromium under Microwave Sintering

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## ABSTRACT

Chromium (Cr) salts have been widely used in various industries and the discharged waste has caused soil contamination. Among them, Cr(VI) is the main concern due to its high solubility and strong carcinogenic properties. This paper compares the performance of a novel microwave sintering technique with the conventional sintering technique for immobilising Cr contaminated soil. The most significant advantage of the microwave sintering is that it can provide controlled atmosphere (such as reduction atmosphere), which means Cr(VI) can be reduced to less hazardous Cr(III) during the sintering process. The potential secondary contamination can, thus, be significantly reduced. The XRD results show that with microwave sintering, stronger and sharper peaks were observed, indicating minerals with higher crystallinity have been formed. On the other hand, the SEM results reveal that with conventional electric sintering, the microstructure was dominated by glassy phases, whilst a mixture of glassy and crystalline phases has been identified with microwave sintering. The leaching results show that the contaminated soil processed with microwave has met both British and Chinese leaching standards, and is better than that from the electric sintering technique.

**Key words:** Chromium contaminated soil, Conventional sintering, Microwave sintering

## 1. INTRODUCTION

Chromium salts are widely used in chemical, light, textile and metallurgy industries. However, the contamination caused by chromium has raised serious concerns around the world. In China, the current annual discharge of chromium slag is about 450K tonnes, which has caused nearly 20 million hectares of soil being contaminated, accounting for about 1/5 of the total cultivated land (Wang, 2011). Chromium exists in environment primarily in two oxidation states: Cr (III) and Cr(VI). Compared to Cr (VI), Cr (III) is less soluble and only becomes toxic at high concentrations. However, Cr (III) is prone to be oxidized to Cr (VI), which has a strong carcinogenic and mutagenic property and high solubility. Furthermore, as Cr (VI) can easily enter the natural water system through scouring, infiltration and surface runoff, Cr (VI) is, thus, considered to be the most severe type of Cr contamination.

Two main approaches have been generally adopted to remedy the soil contaminated by Cr: one is to remove it from the contaminated soil using techniques such as washing, planting selective plants, etc. The limitation of this method is that it may take quite a long time and can cause some secondary contamination (Li, 2011). The

other approach is to convert Cr into insoluble and/or less hazardous forms (Shakoori *et al.*, 2010; Sankaranarayanan *et al.*, 1986). Following the remediation by the second approach, some researchers (Xu *et al.*, 2008; Yang, 2012; Shi, 2013) have attempted to sinter the Cr contaminated soil in order to incorporate Cr into the Si-O or Al-O structure. This has been considered to be a more stable form of stabilization of Cr. However, the conventional sintering technique requires an excessive supply of oxygen, which favors the formation of more hazardous Cr(VI). In this paper, we report using microwave sintering technique to immobilise Cr contaminated soil. Compared with conventional electric furnace, microwave sintering technique has various advantages such as better heat diffusion, less time needed to reach the sintering temperature, less heating energy required and improvements in the product properties (Oghbaei and Mirzaee, 2010). For Cr Immobilisation, in particular, microwave sintering can provide controlled atmosphere, such as the reduction atmosphere, which means whilst Cr can be potentially incorporated into the Si-O-Al structure, at the same time, the more hazardous Cr (VI) could be reduced to less hazardous Cr(III) (Tai and Jou, 1999). The main purpose of this study is, thus, to compare the performance of microwave

sintering with conventional sintering technique for remediating Cr contaminated soil.

## 2. EXPERIMENTAL

### 2.1 Materials

Shale from Shiyan, Hubei province, China, with a moisture content of 1.2% and particle size  $\leq 0.15$  mm, was used as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  source. Its chemical composition is shown in Table 1. Iron oxide was used as a microwave absorbing material in order to achieve the target temperature. Activated carbon powder was used as reducing agent and pore forming agent whilst potassium dichromate as the Cr(VI) source. Both were chemical grade from Sinopharm Chemical Reagent Co., Ltd (China).

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	CaO	$\text{K}_2\text{O}$	MgO	$\text{TiO}_2$	$\text{P}_2\text{O}_5$	Loss
	52.24	18.39	6.87	4.27	2.64	2.55	0.95	0.31	11.15

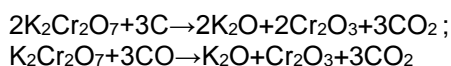
### 2.2 Equipment and Test Methods

A microwave sintering furnace with an output frequency  $2450 \pm 50$  MHz and an output power  $\leq 15$  KW, together with SiC crucibles, were used during the sintering process. The conventional sintering, simulated by an electric furnace with a power output of 55 KW, was used as a control.

The shale was dried in an oven at  $105^\circ\text{C}$  and ground for 20 min in a ball mill to obtain the particle size  $\leq 0.15$  mm. The ground shale was then mixed with iron oxide and carbon powder to form the raw meal to be sintered. Table 2 shows the composition of the raw meal used in this study.

raw material	Shale	$\text{Fe}_2\text{O}_3$	C	Cr(VI)
Ratio (%)	97.895	0.979	0.979	0.147

The raw meal was firstly mixed with water at a water/powder of 0.12 before forming balls of 5 mm diameter. The balls were then aged for 24 hours before being pressed into pellets ( $\phi 50\text{mm} \times 12\text{mm}$ ) under a pressure of 30 MPa for 5 seconds. The formed pellets were then left in oven at  $105^\circ\text{C}$  until constant weights being achieved. Half of these pellets were transferred to the microwave furnace (MF) and the other half to the electric furnace (EF). For both furnaces, the sintering temperature was kept at  $1200^\circ\text{C}$  for 20 mins. However, the EF was under an oxidation environment by flushing air, while the MF was under a reduction atmosphere by adding activated carbon to produce CO. The reactions in the MF can convert Cr(VI) to Cr(III) through a reduction reaction as follows (HJ 2017 - 2012, China standard):



Leaching test was carried out with the formed ceramic pellets which were first crushed to particle size  $\leq 5$  mm. 40g sample was added into 400ml of acidic solution (sulfuric acid and nitric acid with a mass ratio of 2: 1.), and was shaken on a horizontal oscillator for 24h. Leachate was filtered by a  $0.22\mu\text{m}$  filter membrane and the total Cr (Cr(VI) + Cr(III)) was analysed by ICP. The Immobilisation rate (H%) was calculated as follows, where:

- $A_0$ : weight of Cr (mg) in 1g of sample;
- $A_1 = 1.47$  mg/g sample
- $A_2$ : Cr in leachate (mg) per gram of sample;

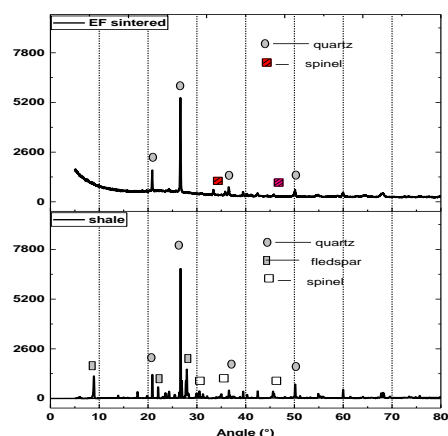
$$A_2 = A_1(\text{Cr in leachate mg/L}) \times \text{volume of solutions(L)} / 40\text{g} = A_1 \times 0.4 / 40 = A_1 \times 0.01 \text{ mg/g sample}$$

Therefore, Immobilisation rate can be calculated as:  $\text{H}\% = (A_0 - A_2) / A_0 \times 100\%$

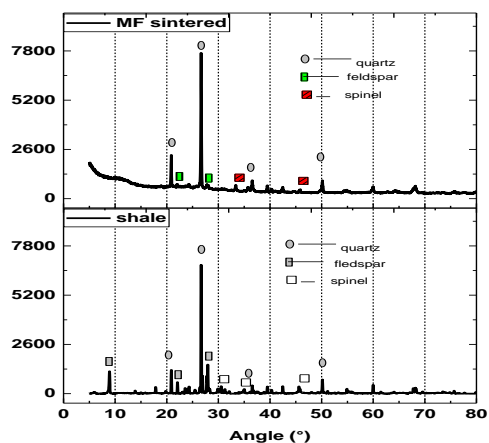
XRD (D8-Advance, BRUKER) was applied to study the crystal phases in the ceramic pellets and SEM (XL30, Philips-FEI) was employed to investigate the morphology.

## 3. RESULTS

### 3.1 XRD Test



(a) EF under oxidation

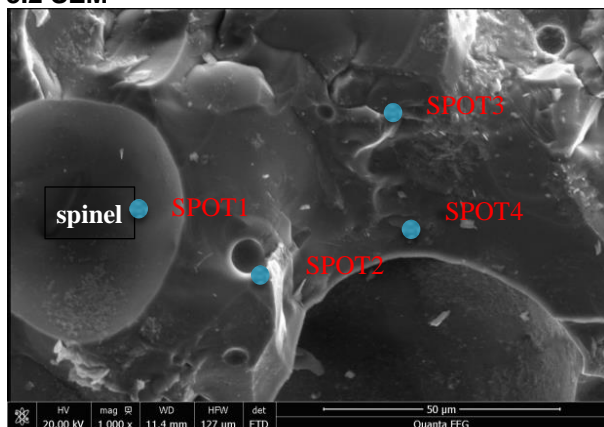


(b) MF under reduction

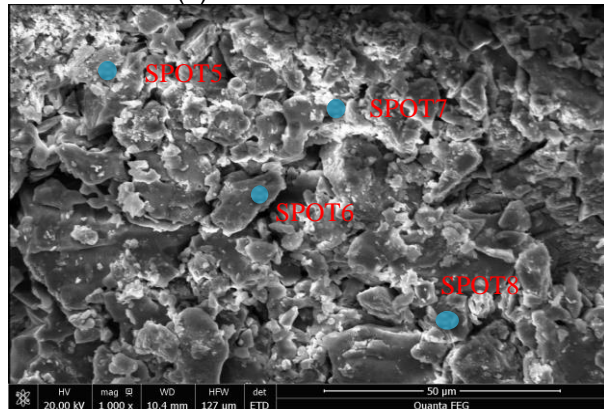
Fig.1 The XRD patterns of sintered products

Fig.1 shows the XRD pattern of the ceramic products under different sintering conditions. The major phases in both patterns are quartz ( $\text{SiO}_2$ ), spinel ( $\text{Mg, Al}$ ) ( $\text{Cr, Al}$ )  $_2\text{O}_4$  and feldspar ( $\text{Ca, K}$ ) ( $\text{Al, Cr}$ )  $_2\text{Si}_2\text{O}_8$ . Comparing with shale, it is clearly shown that Cr is incorporated into product structure by partially replace Al. It has been reported (Xiang and Xie, 2001) that Cr can be fixed in the spinel structure of oxygen octahedral or tetrahedral, and similar results were reported by Aguilar-Rios G (Aguilar-Rios *et al.*, 1992) Compared with EF sintering, MW sintering shows sharper and stronger peaks, indicating that the incorporation of Cr has led to the formation of better crystallized structure.

### 3.2 SEM



(a) EF under oxidation



(b) MF under reduction

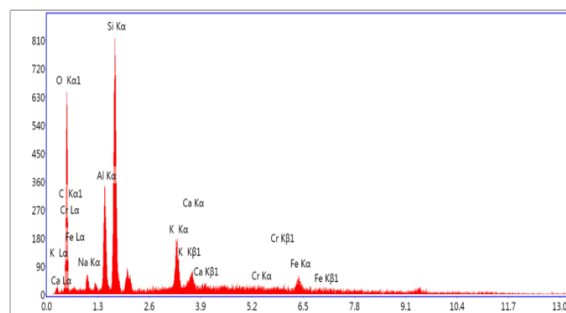
**Fig.2 SEM images of sintered products**

Fig.2 shows that with EF sintering, the microstructure was mainly dominated by glassy phases, whilst a mixture of glassy and crystalline phases has been identified with microwave sintering.

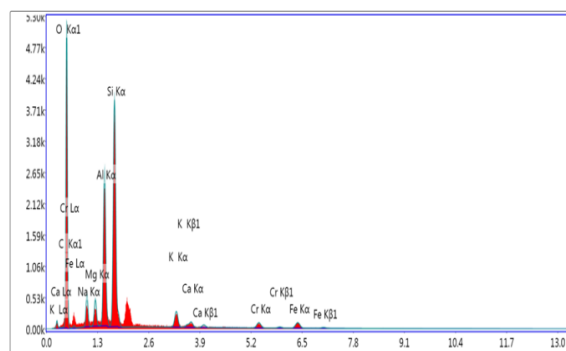
It is generally believed that under conventional sintering, when heated, the powder becomes sticky before reaching its melting point (Tammann *et al.*, 1925). In the present system, the melting points of K-feldspar stone, anorthite, quartz and spinel are:  $1150 \pm 20$  °C, 1550 °C, 1750 °C and 2100 °C respectively (Caniglia and Barna, 1992). Therefore, under conventional sintering, SEM shows a number of round or irregular shape of the

spinel grains observed disseminating in the 10-20 micron silicate liquid phase (Dong, 2012). in the microwave sintering process, due to different microwave absorbing capacities of different raw materials, higher absorbing capacity material takes more heat to form a molten state, while lower absorbing capacity material heated slowly (Tyagi and Lo, 2013). Therefore, a mixture of glassy and crystalline phases was observed.

EDS also confirms that Cr was incorporated into the glassy and crystalline phases under the both sintering technologies.



(a) EF under oxidation (spot1)



(b) MF under reduction (spot6)

**Fig.3 The EDS of EF sintered**

### 3.3 Leaching of total Cr

**Table 3 Leaching of total Cr**

Sintering Method	Atmosphere	Leaching/ mg/g	Immobilization rate /%
EF	oxidation	0.01193	92.05
MF	reduction	0.00290	99.81
British standard (BS EN 12457)		0.01	/
Chinese standard (GB 5085.3-2007)		0.015	/

Table 3 presents the results of the total Cr leached out from the ceramic pellets sintered at 1200 °C under different redox atmosphere for 20 mins. From the results, it can be seen that the EF sintered material can meet the requirements of Chinese Standard (GB5085.3-2007) but cannot meet the British standard (BS EN 12457). However, under the MF sintering, leaching of the total Cr was lower than that from the EF and can meet both the requirements of the British and Chinese relevant standards. In particular, it should

be noted that the lowest value reached 0.00290mg/L in the microwave reduction sintering atmosphere, and the total Cr Immobilisation rate was 99.81%.

Under the reducing atmosphere, the leaching of Cr from the products obtained by microwave sintering was lower than that by conventional sintering under the oxidizing atmosphere. This could be attributed to the significant reduction of the solubility of Cr (III) as compared to that of Cr(VI). Also, it is reported that (Yoshiie *et al.*, 2002) reducing atmosphere can facilitate the incorporation of Cr into the silicate network structure.

#### 4 CONCLUSIONS AND FUTURE WORKS

Microwave sintering technology has been applied to immobilise Cr contaminated soil under reduction environment. The MF and EF sintering mechanisms were investigated and compared. In both cases, Cr was incorporated into the crystal structure as confirmed by XRD. However, under MF stronger and sharper peaks were observed, indicating higher crystallinity. SEM results reveal that under EF, the microstructure was mainly glassy phases, while under MF, the microstructure was a mixture of glassy and crystal phases.

MF has shown better immobilization performance than that of EF within 20min sintering. The total Cr leaching value of the products sintered by MF can meet BS EN 12457, while the sample sintered by EF cannot meet this standard. In addition, a great advantage of MF is the process atmosphere can be controlled, which benefit of converting Cr(VI) to Cr(III) in this application. Therefore, the potential risk of secondary contamination of Cr contaminated soil is significantly reduced.

The analysis of Cr(VI) and Cr (III) by XPS in leachates is on-going, it will be reported once available. Furthermore, it would be interesting to investigate the ratio and distribution of Cr(VI)/Cr (III) in the formed ceramic pellets. Further optimization of MF sintering process will be studied and the loading capacity of Cr will also be investigated.

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