

Equilibrium Phase Relations in the $\text{Al}_2\text{O}_3\text{--CaO--Cr}_2\text{O}_3$ System in Air

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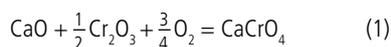
Cr_2O_3 can be present in refractory monolithic castables either as a specific addition or as a residual element present in certain raw materials. The transformation of Cr(III) to Cr(VI) during the use of refractory monolithics can cause subsequent problems with disposal of the used refractory lining. It is therefore important to study the degree of Cr(VI) formation as well as its formation mechanism from a fundamental perspective. This study investigated a simplified system of Al_2O_3 and CaO in the presence of Cr_2O_3 , representative of a system commonly found in refractory castables. Equilibrium phase relations in the $\text{Al}_2\text{O}_3\text{--CaO--Cr}_2\text{O}_3$ system in air were investigated in this study. Samples were prepared by varying the Al_2O_3 contents in the range of 50–80 mass-%. Cr_2O_3 concentrations up to 4 mass-% and equilibrium temperatures up to 1573 K were used. After equilibrium was reached, the samples were quenched in liquid nitrogen. The phases in the quenched samples were studied using XRD analysis. The results indicated that a Cr(VI)-containing phase $\text{Ca}_4\text{Al}_6\text{CrO}_{16}$ with a hauyne crystal structure forms in this system. The water soluble Cr(VI) in the quenched samples was quantified using the diphenylcarbazide spectrophotometric method according to the TRGS 613 standard. The water soluble Cr(VI) in all samples exceeded the allowable European limit.

1 Introduction

In nature chromium mainly exists as chromite, which is a complex spinel (Fe^{2+} , Mg) (Cr,Al,Fe^{3+}) $_2\text{O}_4$, in which chromium is pre-

sent as Cr(III) [1]. Cr(III) is not toxic and relatively immobile [2]. Cr(VI) however, is widely known to be a human carcinogen, mutagenic, allergenic, toxic and can cause contact dermatitis [3]. It is also highly mobile due to its high solubility in water, and can easily contaminate soil and groundwater. The safe disposal of any Cr(VI) wastes is therefore a matter of great concern.

It is known that Cr_2O_3 in the presence of CaO is oxidized at temperatures in the order of 800 °C to CaCrO_4 according to the following reaction [4, 5]:



Kaiser et al. investigated phases relations in the CaO-rich section of the CaO– $\text{Al}_2\text{O}_3\text{--Cr}_2\text{O}_3$ system in air, and found a ternary intermediate phase, chrome-hauyne $\text{Ca}_4[(\text{Al,Cr}^{3+})_6\text{O}_{12}](\text{Cr}^{6+}\text{O}_4)$, coexisted with calcium chromate (CaCrO_4) and calcium aluminate phases [6]. Mizuhara et al. also reported that CaCrO_4 and $\text{Ca}_4\text{Al}_6\text{CrO}_{16}$ could coexist [7]. These two hexavalent chromium-containing phases formed in waste melting furnaces through the reac-

tion between CaO-containing slag and Cr_2O_3 -containing refractories.

Castables that contain Cr_2O_3 are typically exposed to oxidizing conditions during shut down. It is therefore of great importance to investigate equilibrium phase relations in typical castable compositions within the $\text{Al}_2\text{O}_3\text{--CaO--Cr}_2\text{O}_3$ system, to identify the Cr(VI)-containing phases that form in this system, as well as the leachabilities of these phases in water.

2 Experimental

2.1 Raw materials and sample preparation

Based on typical calcium alumina cement compositions, four samples with Al_2O_3 contents from 50–80 mass-%, each containing a fixed amount of 4 mass-% Cr_2O_3 , were used in the equilibrium experiments (Tab. 1). High purity chemicals were employed as raw materials (Tab. 2). The CaO and Al_2O_3 powders were pre-treated before use by calcining them at 1273 K for 10 h in a muffle furnace in order to decompose any hydroxide and carbonate phases that might

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be present. The Cr_2O_3 powder was heat-treated at 383 K for 10 h in order to remove any moisture. The pre-treated oxides were then weighed in different proportions and thoroughly mixed in a tungsten carbide mill, after which the raw materials were pressed into pellets, 20 mm in diameter.

2.2 Equilibrium experiments

Equilibrium experiments were carried out in a MoSi_2 -heated muffle furnace, controlled by a Toho TTM-339 controller equipped with a type-B (Pt-Rh30 %/Pt-Rh6 %) thermocouple. Each sample was placed on platinum foil in the centre of the furnace where the temperature deviation was less than ± 2 K. The sample was heated to 1573 K and equilibrated for 16 h in air. In order to ensure the charges are homogeneous, several heating and grinding cycles were carried out until the X-ray powder pattern remained unchanged. After the last heating period, the sample was quenched by quickly immersing it into liquid nitrogen.

2.3 Analysis

The quenched samples were analysed by XRD using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and with Fe filtered $\text{Co-K}\alpha$ radiation ($\lambda = 1,789 \text{ \AA}$). Phase identification was done using PANalytical X'Pert Highscore plus software, while the relative phase amounts were estimated using the Rietveld method (X'Pert Highscore plus software). The leachability of Cr(VI) was evaluated according to the TRGS 613 standard method [11]. This method is used for the determination of water-soluble chromium(VI) compounds in products that contain cement. 2,5000 g of milled sample ($<0,074 \text{ mm}$) was suspended in 40 ml of distilled water, vigorously stirred for 15 min with a magnetic stirrer (stirrer bar 40 mm, 300 rpm) and then filtered through $0,45 \text{ }\mu\text{m}$ membrane filters. The Cr(VI) content in the leachate was determined with the 1,5-diphenylcarbazide method. A PerkinElmer Lambda 25 UV Spectrometer, using WinUV software, was used for the absorbance measurements.

3 Results and discussion

3.1 Phases relations

Samples of different colours were formed in the equilibrium experiments (Fig. 1). It

Tab. 1 Compositions of the four samples

No.	Compositions [mass-%]		
	Al_2O_3	CaO	Cr_2O_3
1	50	46	4
2	60	36	4
3	70	26	4
4	80	16	4

Tab. 2 Purity grades and supplier of chemicals employed as raw materials

Chemical	Purity [mass-%]	Supplier
Al_2O_3	99,99	Sigma-Aldrich, Germany
CaO	99,9	Sigma-Aldrich, Germany
Cr_2O_3	99,9	Sigma-Aldrich, Germany

is known that chromium (III) oxide is dark green, chromium (VI) oxide is yellow and Al_2O_3 with some Cr_2O_3 in solid solution has a ruby colour. It can therefore be deduced that chromium (III) oxide has been oxidized into Cr(VI) in samples 1, 2 and 3 (50 %, 60 % and 70 % Al_2O_3 , respectively).

The binary Al_2O_3 -CaO phase diagram is presented in Fig. 2 [12]. According to this phase diagram, it is expected that C_{12}A_7 ($12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$) would be the main phase and CA ($\text{CaO} \cdot \text{Al}_2\text{O}_3$) the minor phase in sample 1, CA the main and C_{12}A_7 the minor phases in sample 2, CA and CA_2

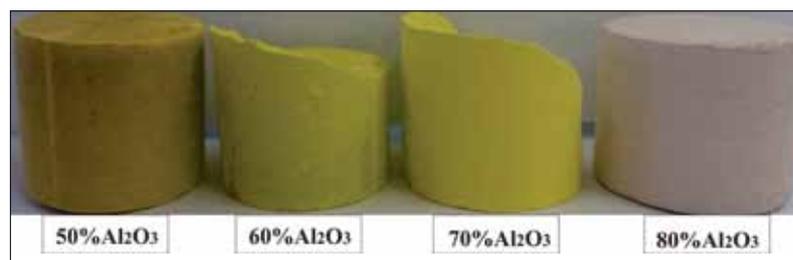


Fig. 1 Samples after being quenched in liquid nitrogen

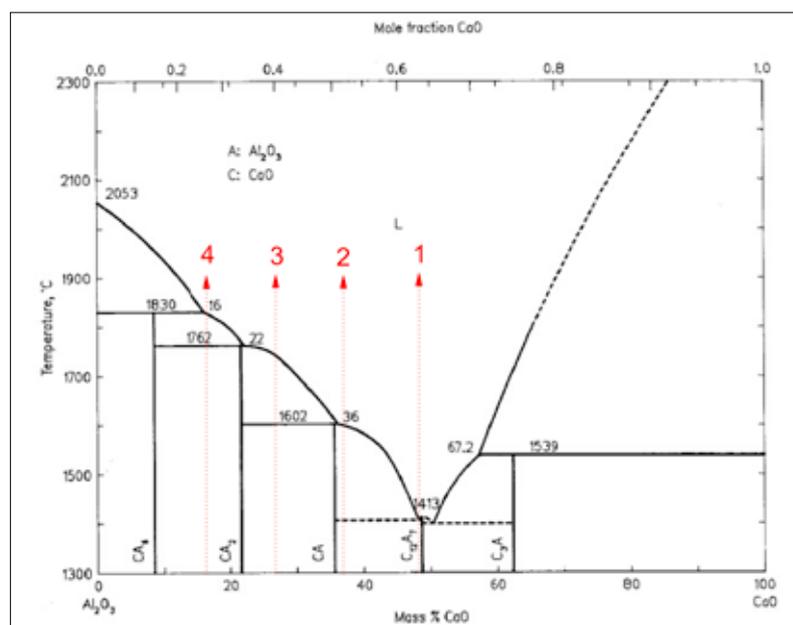


Fig. 2 Phase compositions of the four examined samples, normalised to the binary Al_2O_3 -CaO system

Tab. 3 The estimated phase compositions using the X'Pert Highscore plus software

No.	Phases Composition [mass %]					
	C ₃ A	C ₁₂ A ₇	CA	CA ₂	CA ₆	Ca ₄ Al ₆ CrO ₁₆
1	10,96	59,53	–	–	–	29,51
2	–	0,56	68,92	–	–	30,52
3	–	–	–	73,39	–	26,61
4	–	–	–	58,17	41,42	0,41

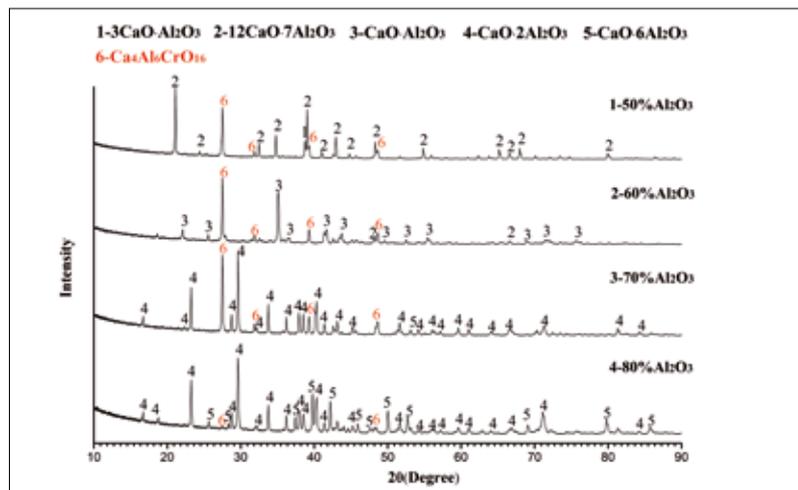


Fig. 3 X-ray diffraction patterns of quenched samples

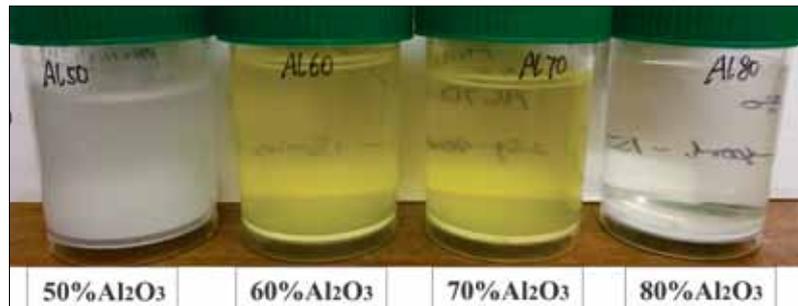


Fig. 4 Filtrate solutions from the TRGS 613 test

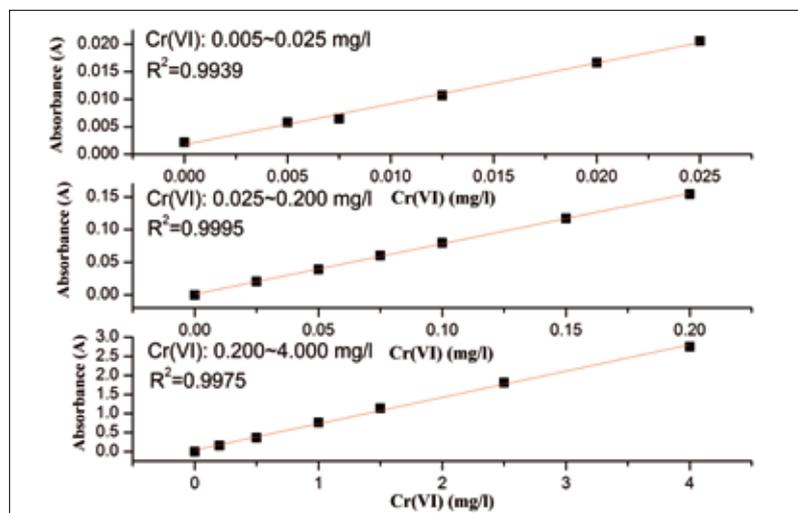


Fig. 5 Three calibration curves for determining the Cr(VI) concentration

(CaO · 2Al₂O₃) the main phases in sample 3, and CA₂ and CA₆ (CaO · 6Al₂O₃) the main phases in sample 4.

X-ray diffraction analysis confirmed that 12CaO · 7Al₂O₃ was the main phase that formed in sample 1 (50 % Al₂O₃), CaO · Al₂O₃ in sample 2 (60 % Al₂O₃), CaO · 2Al₂O₃ in sample 3 (70 % Al₂O₃) and a combination of CaO · 2Al₂O₃ and CaO · 6Al₂O₃ in sample 4 (80 % Al₂O₃) (Fig. 3).

The main change in phase relations caused by the addition of 4 % Cr₂O₃ to the Al₂O₃-CaO system is the formation of a Cr(VI)-containing phase Ca₄Al₆CrO₁₆, which has a hauyne crystal structure. Hauyne was observed as the main secondary phase in samples 1, 2 and 3 (50 %, 60 % and 70 % Al₂O₃) but was present in trace amounts in sample 4 (80 % Al₂O₃). The presence of the Cr(VI)-containing Ca₄Al₆CrO₁₆ can explain the yellow colour of samples 1–3 (50 %, 60 %, 70 % Al₂O₃).

The AUTOQUAN program can be used for accurate quantitative XRD phase analysis by the Rietveld method. Unfortunately, due to a lack of crystallographic data on the hauyne phase in the database, the amount of this phase could only be estimated by using the X'Pert Highscore Plus software, and crystal structure data of hauyne at 463 °C [13].

Quantitative XRD confirmed high concentrations (>26 mass-%) of Ca₄Al₆CrO₁₆ in samples 1–3 (50 %, 60 % and 70 % Al₂O₃), while only 0,41 mass-% in sample 4 (80 % Al₂O₃). Structural data of pure hauyne needs to be generated in order to conduct accurate quantitative analysis with AUTOQUAN in future.

3.2 Leach test

The extraction of hexavalent chromium was evaluated according to the TRGS 613 procedure. In order to get enough leach solution, 40 ml distilled water (L/S ratio: 16/1) was added during the leach test. The filtrates obtained from the different samples were different in colour (Fig. 4). The leach solutions of samples that contained 60 and 70 % Al₂O₃ were very yellow (samples 2 and 3), which implied that the solutions should contain significant amounts of Cr(VI).

In order to accurately determine the Cr(VI) in different concentrations, three calibration curves in the ranges of 0,005–0,025 mg/l,

0,025–0,200 mg/l and 0,200–4,000 mg/l were prepared (Fig. 5).

The Cr(VI) concentrations leached from samples 1, 2, 3 and 4 (50 %, 60 %, 70 % and 80 % Al₂O₃) were 0,75 mg/l, 127,21 mg/l, 188,76 mg/l and 4,64 mg/l, respectively (Fig. 6).

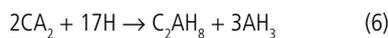
The following equation can be used to calculate the mass percentage of water soluble Cr(VI) in the quenched samples:

$$Cr(VI)_{\text{soluble}} [\%] = \frac{C \times V \times 10^{-6}}{m} \times 100 \quad (2)$$

where C [mg/l] is the concentration of Cr(VI) in the leach solution; V [ml] is the volume of distilled water added; m [g] is the mass taken from the quenched samples. The amount of water soluble Cr(VI) in quenched samples 1, 2, 3 and 4 were 0,0012 mass-%, 0,2035 mass-%, 0,3020 mass-% and 0,0074 mass-%, respectively (Fig. 7). However, the water soluble Cr(VI) in cement is limited to 0,0002 mass-% according to European Standards [14]. The water soluble Cr(VI) in all samples were substantially higher than the allowable limit.

A substantial difference in the percentage of Cr(VI) that leached from the four samples with different Al₂O₃/CaO ratios was observed. This indicates that the presence of different types of hydrated phases directly influence the leachability of Cr(VI).

The hydration processes of the calcium aluminate phases C₃A, C₁₂A₇, CA, and CA₂ proceed according to the following reactions [15]:



He and Suito [16] demonstrated that Cr(VI) can be immobilised by hydrated calcium aluminates and the AFm phases of C₃A · Ca(OH)₂ · xH₂O through the substitution of the CrO₄²⁻ ion for OH⁻. According to Eq. (3) and (4), C₄AH₁₃ is generated first during the hydration process of C₃A and C₁₂A₇. Since only a small amount of Cr(VI) was leached from sample 1, immobilisation of Cr(VI) by specifically the C₄AH₁₃ phase must be further explored.

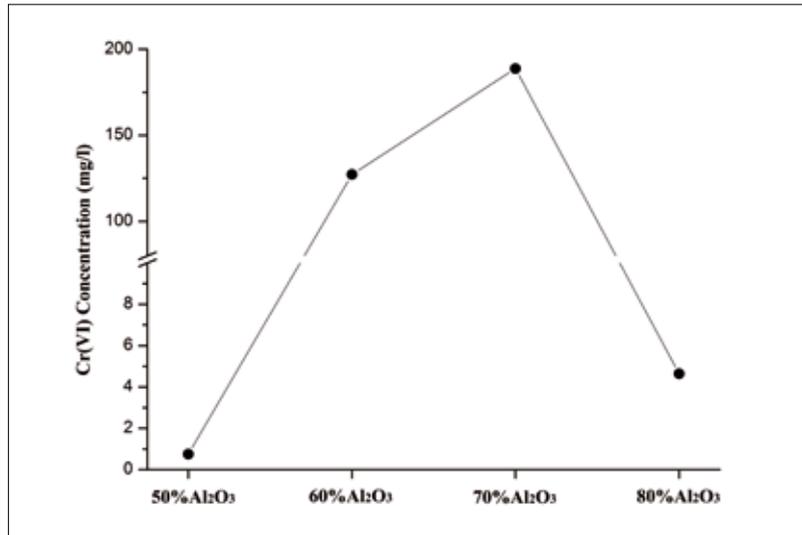


Fig. 6 Cr(VI) concentrations in the four leach solutions

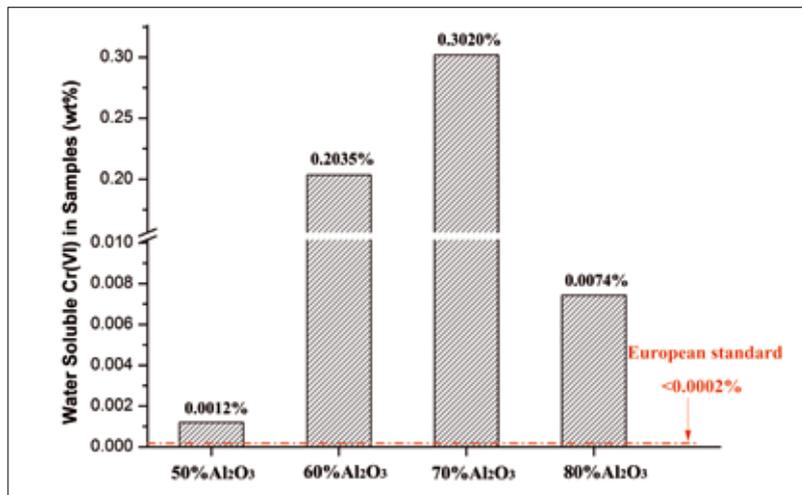


Fig. 7 Mass percentage of water soluble Cr(VI) in the examined quenched samples

4 Conclusions

- (1) A Cr(VI)-containing phase Ca₄Al₆CrO₁₆ with a hauyne crystal structure, forms in the Al₂O₃–CaO–4 mass-% Cr₂O₃ system in air.
- (2) Ca₄Al₆CrO₁₆ formed in samples that contained 50 %, 60 %, and 70 % Al₂O₃ respectively. Only trace amounts of Ca₄Al₆CrO₁₆ formed when the sample contained 80 % Al₂O₃.
- (3) The amount of water soluble Cr(VI) in all quenched samples that contained 50 %, 60 %, 70 %, and 80 % Al₂O₃ respectively exceeded the allowable European limit.
- (4) The hydration processes associated with the observed C₃A, C₁₂A₇, CA, and CA₂ phases significantly affect the leachability of Cr(VI).

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