

LEACHABILITY OF CHROME FROM MAGNESIA-CHROMITE REFRACTORY BRICKS CORRODED BY Cu/CuO-Na₂O·2SiO₂ SLAGS

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The interactions of magnesite-chromite refractory brick with Cu-Na₂O·2SiO₂ and CuO-Na₂O·2SiO₂ melts are studied and the chemical durability of corrosion products in water is evaluated. The corrosion tests confirm intensive infiltration of the slag melts into the tested refractory bricks and formation of Cr(6+) compounds. The molten copper partially oxidizes during corrosion test by air and penetrates into bricks. Interactions among periclase (MgO) and chromite (FeCr₂O₄) grains with the melt Na₂O·2SiO₂ and copper oxides makes possible to form several compounds (e.g. Cu₂MgO₃, CuCrO₄, CaCrO₄, Na₂CrO₄, MgCrO₄). Just the marked yellow spots, which were observed on the corroded brick surface after 30 days of free storage, suggest hydration of the high-temperature corrosion products. The yellow color of spots points out to chromates as Na₂CrO₄ and MgCrO₄, which are well soluble in water. The leaching of corroded bricks in water (batch leaching test of a ratio of S (solid) : W (water) = 0.1 taking up to 28 days) confirmed the Cr, Na, Mg and Ca ions leach-out. The pH value of solution increased up to 9 during leaching mainly as a consequence of elevated Na⁺ ion concentration. The Cr ion concentration rises in the solution up to 1 mmol·l⁻¹. The observed moderate decrease of Cr ion concentration in the solution with the length of leaching indicates super-saturation of the solution and precipitation of the products.

INTRODUCTION

The working lining of copper refining (anodic) furnace made of magnesite-chromite (MCr) refractory materials is exposed to high temperatures and aggressive slags. The fire refining process of copper is in term of corrosive effect extreme, thermal shocks occur and redox-potential changes at a temperature of 1200°C in the furnace atmosphere. All refining process takes about 24 h, of this the oxidizing period lasts about 4 h, the reducing period about 3 h, and batching of raw materials and anode casting occurs in the remaining time.

The properties vs composition of working lining, the corrosion processes and the corrosion products are studied consecutively, also on account of their recycling, safer disposal of used bricks and dumping conditions [1-7].

The recycling of used furnace lining from pyrometallurgical aggregates is technologically and economically very difficult; therefore the used refractory bricks end largely on waste dump. The waste bricks from the furnace lining and refractories from metallurgy with chrome compounds come under hazardous wastes category. Cr⁶⁺ compounds can be created in interaction of chromite and magnesite-chromite refractory bricks with reactive slag as Na₂O-SiO₂ [1, 2, 5-8].

The dumping of this refractory debris is a serious problem, as it is a potentially hazardous waste to human health and all ecosystem, water, soil, plants and animals. The debris step by step disintegrates at the dump and the corroded magnesite-chromite bricks are dissolved by rain and ground water. The risk of water contamination by heavy metal ions, mostly by Cu and Cr ions, is high. The toxicity of Cr^{3+/6+} compounds is in connection with their solubility. The Cr³⁺ compounds are less soluble than the Cr⁶⁺ compounds therefore the Cr⁶⁺ ion is extra-hazardous for health. The trivalent Cr³⁺ is not generally considered toxic. The Cr⁶⁺ compounds are classified as very toxic pollutants and carcinogens at which the dichromates are more toxic than chromates. The limit of Cr⁶⁺ concentration in mining water at working, ores processing and the limit for underground and surface waters are provided by laws of the individual countries [9-10]. The limit of Cr concentration in mining water in Slovakia provided by law [11] is 0.1 mg·l⁻¹

This article focuses on dumping risk of used magnesite-chromite brick from refining furnace through the evaluation of corrosion products leachability by water. The commercial refractory magnesite-chromite bricks were corroded by artificial Cu-Na₂O·2SiO₂ and CuO-Na₂O·2SiO₂ slag melts. The corrosion tests were carried out by static crucible test in electric resistance furnace at

a temperature of 1350°C/10 h in air. The penetration and interaction of melted slag with bricks were interpreted from the macro- and microstructure and composition of corroded bricks.

The corroded bricks leaching was carried out as batch test at ratio S(solid) : W(water) = 1 kg : 10 l for a period of 28 days. The chemical instability of corrosion products in water was evaluated from ion concentration in leach in dependence on leaching time.

EXPERIMENTAL

The experimental program is focused on leaching of the corroded magnesia-chromite refractory bricks from the copper refining furnace in water. The crucibles were prepared from the commercially produced of magnesia-chromite bricks (MCr). The average bulk composition and selected properties of tested MCr are given in Table 1. The MCr brick were cut on blocks of size (88 × 88 × 64) mm and then a 30 mm deep hole with 30 mm diameter was drilled into each block. The samples were dried in laboratory drying chamber at a temperature of 110°C for 24 h before corrosion test.

Synthetic slag systems were prepared from: SiO₂ (96.5 %, P.P.H. Polske odczynniki chemiczne, Gliwice, Poland) and Na₂CO₃, CuO (LACHEMA, a.s., Brno, Bohemia) and electrolytic metal Cu (99.95 %, Kovohuty Krompachy, Slovakia). The compounds of corrosion mixes used for the experiments were the following:

1. set MCr 1: 80 g Cu, 4 g SiO₂ a 3.53 g Na₂CO₃;
2. set MCr 2: 25 g CuO, 4 g SiO₂ a 3.53 g Na₂CO₃ (mol. ratio SiO₂: Na₂O = 2).

The hole in MCr crucible was filled up with the corrosion medium, at first metal Cu or CuO was put, next on top the mix of SiO₂ and Na₂CO₃. The loaded MCr crucibles were held in laboratory resistance furnace at a constant temperature of 1350°C (± 5°C) for 10 h. After completion of the tests, the samples cooled in the furnace.

After corrosion test the MCr crucibles were cross cut and the infiltration of corrosion medium was observed. A NEOPHOT 32 optic microscope was used to study the macrostructure on polished blocks and a JEOL JMS 7000F microprobe coupled with an energy dispersive spectroscopy (EDS) system was used to semi-quantitative analysis.

The samples for chemical analysis have been obtained from the corroded crucibles in 5, 20, 30 mm distance from crucible bottom. The samples were decompo-

sed by classical chemical method and a Cr, Cu, Na and Si concentration in solutions was determined by AAS (Elmer Perkin 3100 spectrophotometer).

One part of the samples from corroded bricks was ground by a TMR 2 edge mill. The grain fraction of sample under 0.5 mm was used for two parallel series of leaching tests in distilled water (pH – 5.7) for 28 days. The ratio of solid to water was 50 g : 500 ml, a leaching temperature was 23°C. The suspensions were stirred during the first 60 min and then they were only shortly stirred before each taking of samples and 30 min after stirring 50 ml of water samples were taken for analysis. The samples in glass tanks were covered during leaching tests. The sampling carried in time 2 h and daily for 8 days and last sampling was on the 28 day. The concentration of Cr, Cu, Fe, Na, Si, Al, Mg and Ca in solution was measured by spectrophotometer AAS (Perkin Elmer 3100) after measuring of pH value and acidifying.

A leaching effect (LE) was calculated according to equation:

$$LE_{Me} = \frac{m_{Me(\tau)}}{m_{Me(o)}} \cdot 100 \% \quad (1)$$

where $m_{Me(\tau)}$ - the Me ion concentration in solution volume with correction on previous samplings (mg), $m_{Me(o)}$ - the Me content in leach dose (mg).

RESULTS AND DISCUSSION

Corrosion of magnesia-chromite bricks by Cu/CuO_x·Na₂O·2SiO₂ slag

The Na₂O-SiO₂ slag composition, which was used to the static corrosion tests, is very similar to copper refining slag. The ratio of Na₂O to SiO₂ in slag corresponds to the composition of Na₂O·2SiO₂ compound which melts at temperature of 874°C (Figure 1) [12]. The melting points (t_{liq}) of used (Na₂CO₃ + SiO₂) melt and CuO have been measured by Leitz Wetzlar microscope; $t_{liq}(\text{Na}_2\text{CO}_3 + \text{SiO}_2) = 995 \pm 5^\circ\text{C}$, and $t_{liq}(\text{CuO}) = 1140 \pm 5^\circ\text{C}$.

High temperature of corrosive tests, respectively high overheating of Na₂O·2SiO₂ melt, results in a low viscous melt, and its low surface tension and intensive capillarity in the tested bricks. The low viscous melt slag infiltrated completely the bulk crucible. It must be noted that some oxidation of the copper phase occurred during the high-temperature tests (1350°C) for exposure to ambient air when the copper and slag are melted together.

Figures 2 and 3 give information about the macro-

Table 1. Composition and properties of the tested magnesia-chromite bricks (MCr).

Sample	Composition (wt. %)						Apparent porosity π_a (%)	Bulk density ρ_b (kg·m ⁻³)
	MgO	Cr ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	CaO		
MCr	56.3	25.57	3.91	10.15	1.55	2.48	16.7	3 152

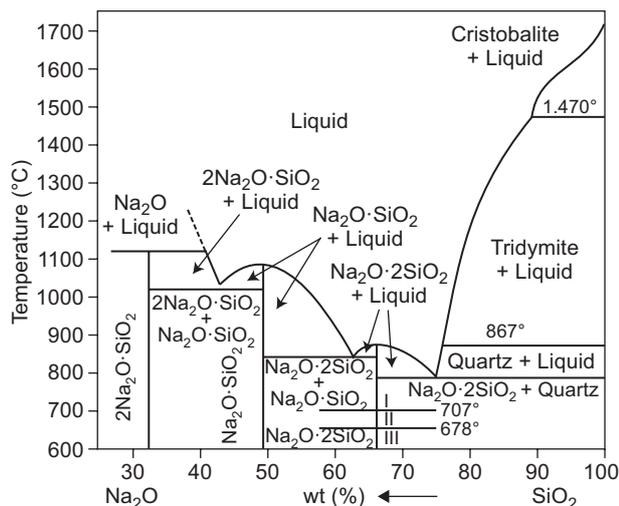


Figure 1. Phase diagram of the system Na₂O-SiO₂ (wt. %) [12].

structure of the MCr sample immediately after corrosion test and after 30 days on ambient-air. On the cut sample one can see the zonal infiltration of corrosive medium (Cu(CuO_x)-Na₂O-2SiO₂) into the matrix of crucible. The two/three zonal penetration of Cu(CuO_x), Na₂O and SiO₂ and the different degree of disruption to crucible block characterize the perceptible color changes. The chemical analyses in Table 2 verified the zonal infiltration of Cu, Na, Si into MCr1 and MCr2 samples.

Top concentration of Cu/CuO_x is on surface inside-wall crucibles (zone 1) and along a bulk of magnesia-chromite sample decreases. This seems to suggest that Na₂O and SiO₂ penetrate the bricks concurrently. The infiltrated slag partially dissolved and reacted with the grains of (Fe,Mg)Cr₂O₄ and MgO in sample – wide as had shown Petkov et al. [2], too. The form of forsterite and complex spinels is typical for high-temperature processes in MgO–CuO–SiO₂–FeO/Fe₂O₃–Cr₂O₃ (Al₂O₃) systems.

The red-brown spots, observable on cut (Figures 2a, 3a), suggest the intensive disruption of brick by Cu/CuO component of corrosive medium. These spots are most evident at the contact zone, e.g. the inside walls of the crucible. The dissolving condition of chromite and periclase and formation of complex compounds (e.g. CuCrO₂, CuCrO₄, CuCr₂O₇ and Cu₂MgO₃) are well in zone with high content of Cu/CuO at a temperature of 1300 °C.

Paranthamana et al. in work [13] studied the solu-

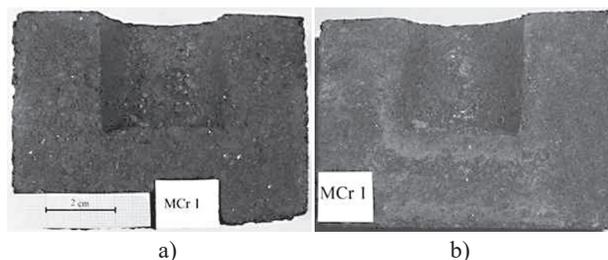


Figure 2. Overview on magnesia-chromite refractory crucible corroded by slag of system Cu-Na₂O·2SiO₂ (sample MCr1): a) sample immediately after corrosion test; b) sample stored on ambient at temperature of 23°C for 30 days.

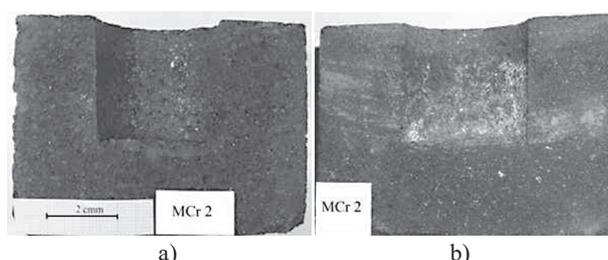


Figure 3. Overview on magnesia-chromite refractory crucible corroded by slag of system CuO_x-Na₂O·2SiO₂ (sample MCr2): a) sample immediately after corrosion test; b) sample stored in ambient air at a temperature of 23°C for 30 days.

bility of CuO in MgO at a temperature < 1 100°C and confirm the solubility of CuO in MgO, which is about 20 % at 1050°C. The higher copper concentration changes the color of the white periclase phase to light yellow. If the CuO content in systems Mg–Cu–O is above 30 wt. % is currently the guggenite (Cu₂MgO₃) crystallization below temperature of 1060°C [13, 14]).

The zonal corrosion becomes more obvious on surface of cut samples after 30 days (Figures 2b, 3b). The color differences between the images a) and b) show the corrosion products probably hydrate in ambient air and the water soluble salts are rising to the surface. The appeared yellow-green and yellow colored zones indicate the high concentration of chromate. In case of MCr1, the clear attack and melt penetration can be seen below surface within crucible, along a bulk of magnesia-chromite sample. Well-marked yellow spots are shown on the surface of the inner side of the MCr2 crucible, in cavities and the less dense part below the surface of refractory, too.

Table 3 provides a solubility and color of selected

Table 2. Zonal element analysis of corroded refractory bricks MCr1 and MCr2 (zone 1 – internal wall of crucible (+ 5 mm), 2 – bulk, 3 – external wall of crucible (+ 5 mm)).

Sample MCr1	Element contents (wt. %)				Sample MCr2	Element contents (wt. %)			
	Cu	Si	Na	Cr		Cu	Si	Na	Cr
MCr1-1	5.58	0.84	0.25	4.99	MCr2-1	4.53	0.64	0.17	4.49
MCr1-2	4.03	0.78	0.58	4.60	MCr2-2	1.33	0.99	0.14	4.94
MCr1-3	0.79	0.82	0.16	4.85	MCr2-3	0.33	1.26	0.14	3.84

chromates, the assumed high-temperature corrosion products Cr^{6+} [15]. The green color is typical for Cr_2O_3 and some chromite compounds. The yellow are sodium and magnesium chromates which are well soluble in water. Dichromates $Na_2Cr_2O_7$ and $MgCr_2O_7$ are soluble in water, too, for dichromate it is characteristic the orange up to red hue [15-17].

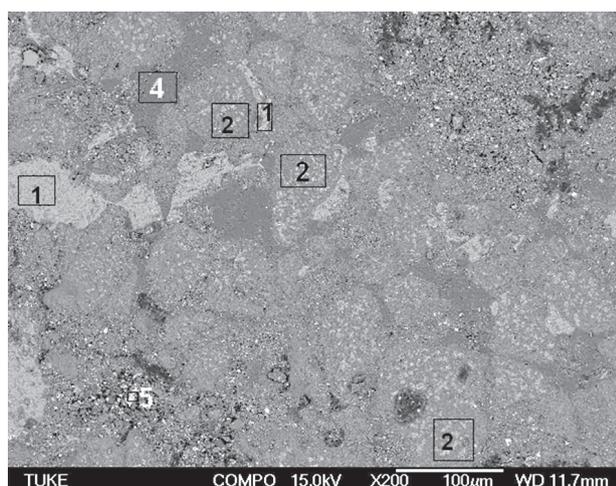
More samples after corrosion tests were analyzed by electron microscope JEOL JSM 7000F. The compositions of grains and mesophases identified by EM-EDS are listed beside the Figures 4a, b. Because the cut patterns were polished under water only non- and less-soluble compounds in water can be identified on surface by the

semi-quantitative analysis. Probably it is the reason why the sodium (Na) element has not been set in the MCr1 sample. In case of MCr2 sample a small quantity of Na was detected locally along with Al and Si.

Between the chemical composition of corroded MCr1 and MCr2 samples there were not any significant differences. Copper was determined at places with dominant presence of Mg and (Mg + Fe) and the molar ratio of Mg : Fe suggest the MgO and $MgFe_2O_4$ phases. Between MgO and $(Mg,Fe)Cr_2O_4$ grains there exist continuous phases including that of Si. These results are in accordance with work of Petkov et al. [2].

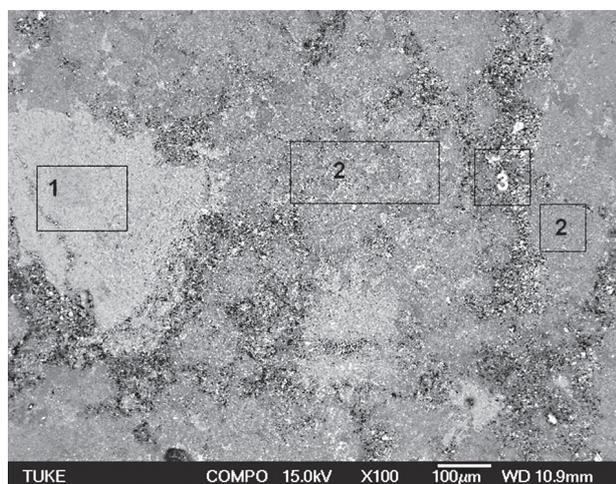
Table 3. Solubility of some chromates in water; (x-solid).

Substance	Na_2CrO_4	$MgCrO_4 \cdot 7H_2O$	$CaCrO_4$	$Fe_2(CrO_4)_3$	$CuCrO_4$
x g/100 g water (20 °C)	84	137	2.25	insoluble	0,035
color	yellow	light yellow	light yellow	yellow	brown



a) $Cu-Na_2O \cdot 2SiO_2$ (MCr 1)

MCr1	At. %			
	1	2	4	5
element				
Mg	19	44	31	13
Cr	21	3	0	3
Fe	6	4	0.2	57
Al	6	1	0	1.5
Ca	0.2	0.1	0.1	0
Si	0.1	0.5	15	0.5
Cu	0.5	4	0	1.2
probable phases	$Mg(Fe)Cr_2O_4$	MgO $(Mg(Fe)Cr_2O_4)$	Mg_2SiO_4	$MgFe_2O_4$



b) $CuO_x-Na_2O \cdot 2SiO_2$ (MCr 2)

MCr1	At. %		
	1	2	3
element			
Mg	18	35	30
Cr	17	2.5	2.5
Fe	4	4	8
Al	5	1.5	3
Ca	0.2	0.3	0.5
Si	0	1.8	1.5
Na	0	0.5	2
Cu	0	1.5	1.5
probable phases	$Mg(Fe)Cr_2O_4$	MgO $Mg(Fe)Cr_2O_4$	MgO $MgFe_2O_4$

Figure 4. Microstructure of magnesia-chromite refractory bricks from reaction zone after corrosion test by melting: a) $Cu-Na_2O \cdot 2SiO_2$ (MCr 1); b) $CuO_x-Na_2O \cdot 2SiO_2$ (MCr 2) with elementary analysis of grains and mesophase; (EM/EDX).

Leaching of Cr from corroded magnesia-chromite bricks

The time dependence results of Cr, Na, Mg and Ca ions leachability from corroded MCr1 and MCr2 magnesia-chromite sample are shown in Figure 5a-d. The first leaching tests are carried out immediately after grinding of the corroded samples and the second tests repeated 14 days after the grinding. The grain refinement by grinding made accessible all corrosion products immediately to water. Nevertheless, the Fe, Si, Al and Cu ion concentrations in leachates keep below the detecting limit of AAS methods (Perkin Elmer 3100).

In principle the corroded magnesia-chromite bricks have been leached in alkali medium. After 2 h of leaching, the pH value in both leaches (from MCr1, MCr2) increased from the initial pH = 5.7 to pH 8.3 – 8.7. In the following 7 days the pH value increased slowly to 8.9 and after 28 days raised to 9.8. The cause of solution alkalinity is Na⁺ which comes from corrosive melt (Na₂O·2SiO₂) and the soluble high-temperature corrosion products. As the calculations show up to 50 % of penetrated Na⁺ into the sample during the corrosion test releases to water in the beginning of leaching but then the Na⁺ concentration increases very slowly. The

solution alkalinity influences the solubility of corroded refractory compounds. The Na⁺, Mg²⁺, Cr^{3+/6+} and Ca²⁺ concentrations in leaches is ranging from 2-2.5; 1.5-2.2; 0.4-1 and 0.15-0.25 mmol·l⁻¹, respectively.

The Cr – leaching time curves of Cr and Ca ions (Figure 5a-b) point to the precipitation, probably less soluble compounds create (Table 3). Unlike Mg²⁺ the Cr^{3+/6+} and Ca²⁺ concentration after maximum concentration achieved by 2-24 h leaching decreases. In comparison of new and old ground samples higher Cr concentrations were detected at the beginning, during the first hours of leaching, in cases of the old samples. The reason may be the hydration at which Figures 2 and 3 of the corroded bulk points out. The following drop of Cr - ion concentration in time-leaching can be the result of slowly progressive of pH value and solution saturation with the (CrO₄)²⁻ anions toward CuCrO₄ and CaCrO₄ as well as oxo/hydroxides Cu and Cr.

The Cr-ion stability in water was determined by model E-pH diagrams which were constructed by HSC7 program [18]. Figure 6 shows the E-pH diagrams of Cr – H₂O system at temperature of 20°C. Existence of Cr - hydroxide complex and Cr - oxo-hydroxide at Cr concentration of 1·10⁻² and 1 mmol·kg⁻¹ is probable within pH = (4 – 10) and as the Cr - concentration in

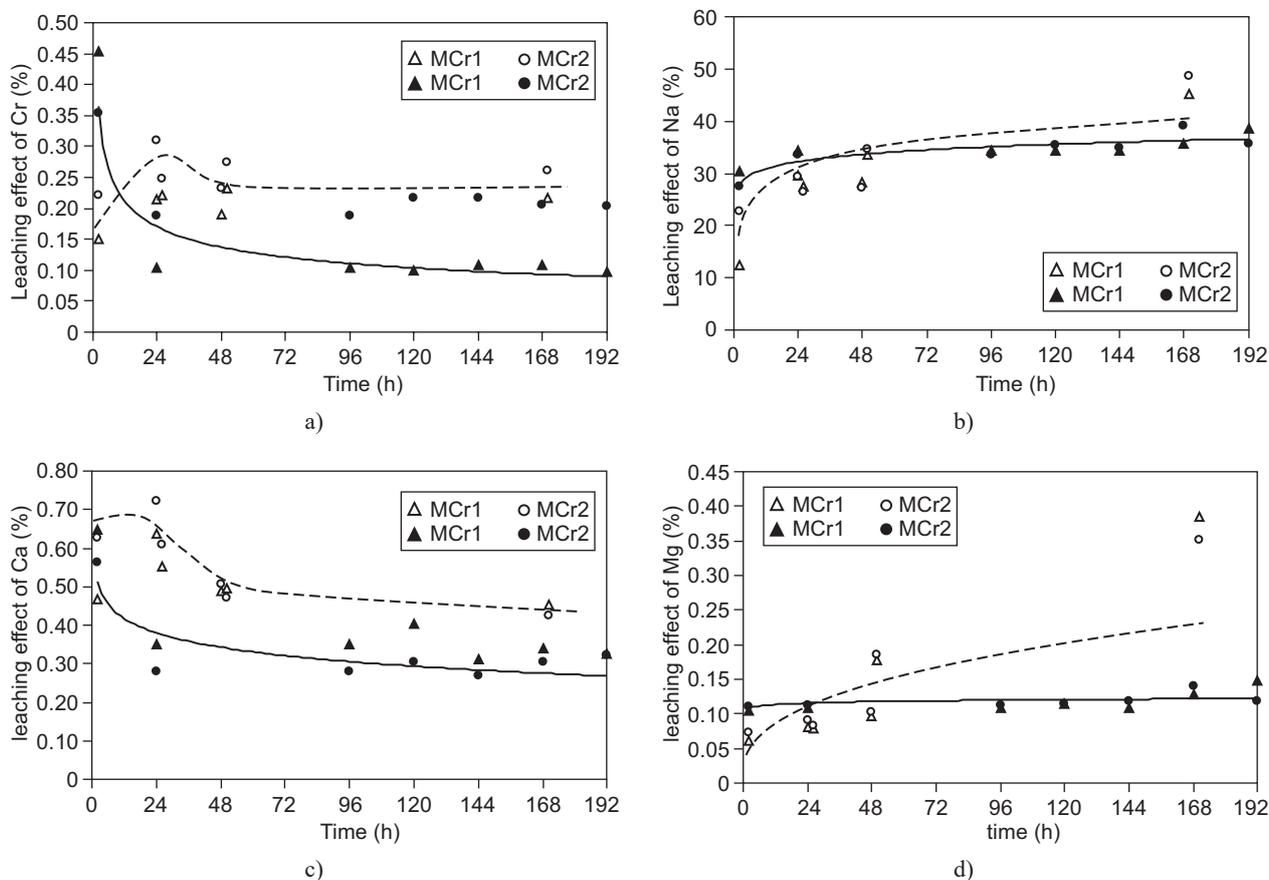


Figure 5. Changes of Cr, Ca, Na and Mg concentration in water with leaching time of corroded samples MCr1 and MCr2; a) Cr, b) Na, c) Ca d) Mg (Δ ○ - corroded samples leached immediately after grinding; \blacktriangle ● - corroded samples leached 14 days after grinding).

system decreases the Cr(OH)₃/CrO(OH) region narrows. At moderate oxidation conditions account must be taken with chromate (Cr⁶⁺) throughout the pH scale.

Probably, the present Ca, Cu, Fe, Al and Si in the refractory bricks create the condition to generation of less soluble and insoluble compound of iron, copper

and calcium. Saturation of leach by Ca²⁺ and Cr^{3+/6+} at pH = 7-10 creates the condition for precipitation. The E-pH diagrams of Cr-Cu-Ca-Mg-H₂O system point to CuCrO₂, Cu(OH)₂, Cr(OH)₃, MgCrO₄ and MgCr₂O₄ compounds at the pH.

The solubility of selected Cr - salts and hydroxides is listed in Table 4, where the ΔG_R^0 value is indicator of the thermodynamic stability of compounds in water. The thermodynamic constant (K) of selected compounds were calculated and compared with the tabulated K_{SP} (solubility constant).

CONCLUSION

The corrosive Cu-Na₂O·2SiO₂ and CuO-Na₂O·2SiO₂ slags have been infiltrated very fast and completely in magnesia-chromite refractory bricks at a temperature of 1350°C. The zonal corrosion with different infiltration of copper and corrosion of MgO and FeCr₂O₄ grains by corrosive slag (alkali and copper oxides) created in 10 h of heating in oxidation conditions. The high temperature corrosion products hydrated in air consequentially manifest themselves on the brick surface by partial colors to yellow. The intensive yellow coloration of the 1st reaction zone with high Cu concentration suggests the presence of new corrosion products, probably chromates.

The leaching tests of corroded bricks confirmed the presence of soluble chromate. Immediately at the beginning of leaching tests together with chromates are released from corroded samples of Na⁺ ions which come from corrosion slag and the pH value of leaching medium moves up. Decrease of Cr and Ca concentration in medium at time-leaching at increase of pH (> 9) suggests the precipitation of Cr and Ca compounds.

Storage conditions of used magnesia-chromite refractory bricks are variable, dependent on weather. In case of standing water the alkalinity and concentration of leachable elements can increase and the brick corro-

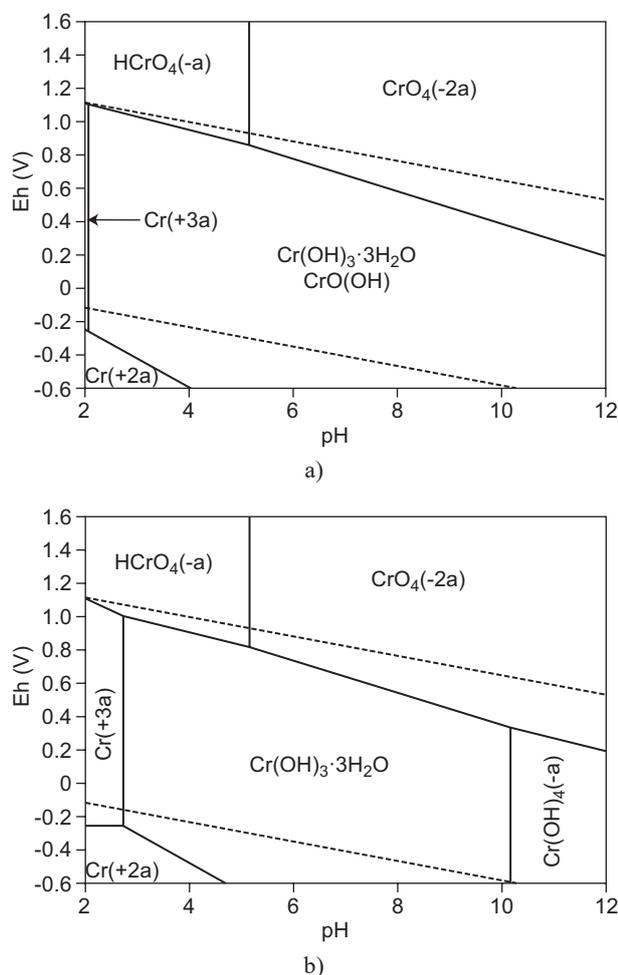


Figure 6. E-pH diagram of Cr compounds in system Cr-H₂O at 20°C; a) concentration of Cr - 1 mmol·kg⁻¹, b) concentration of Cr - 1·10⁻² mmol·kg⁻¹.

Table 4. Thermodynamic stability of some Cr compounds in water and their solubility constants (K_{sp}) [18].

Dissociation equation	ΔG_R^0 (kJ)	Thermodynamic constant K (25°C)	K_{SP} [15, 17]
CuCrO ₂ = CrO ₂ (-a) + Cu(+a)	148.5	9.5·10 ⁻²⁷	
NaCrO ₂ = CrO ₂ (-a) + Na(+a)	30.9	3.9·10 ⁻⁶	
MgCr ₂ O ₄ = 2CrO ₂ (-a) + Mg(+2a)	169	2.9·10 ⁻³⁰	
MgCrO ₄ = CrO ₄ (-2a) + Mg(+2a)	52	7.8·10 ⁻¹⁰	
CaCrO ₄ = CrO ₄ (-2a) + Ca(+2a)	22	1.4·10 ⁻⁴	7.1·10 ⁻⁴
Na ₂ CrO ₄ = CrO ₄ (-2a) + 2Na(+a)	-16.7	8.4·10 ²	
Cr(OH) ₃ = Cr(+3a) + 3OH(-a)	168.8	2.8·10 ⁻³⁰	6.3·10 ⁻³¹
Fe(OH) ₃ = Fe(+3a) + 3OH(-a)	214	2.9·10 ⁻³⁸	6·10 ⁻³⁸
Cu(OH) ₂ = Cu(+2a) + 2OH(-a)	123	2.6·10 ⁻²²	2·10 ⁻¹⁹
Ca(OH) ₂ = Ca(+2a) + 2OH(-a)	30.8	3.9·10 ⁻⁶	5.6·10 ⁻⁶
Mg(OH) ₂ = Mg(+2a) + 2OH(-a)	63.7	7·10 ⁻¹²	1.8·10 ⁻¹¹

sion by alkali will progress by the by precipitation of less soluble compounds. The flow of water through storage will be lower the concentration and alkalinity, at which dissolution of precipitate will be promote. The components will be washed off slowly. Therefore preventive safety measures for used refractory (magnesia-chromite) bricks storage are required to protect pollution of sub- and surface water by heavy metal, mainly Cr⁶⁺.

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