EFFECT OF PARTICLE SIZE DISTRIBUTION AND CHEMICAL COMPOSITION ON PROPERTIES OF MAGNESIA-CHROMITE BRICKS

J. Javadpour

Department of Materials and Metallurgical Engineering
Iran University of Science and Technology, Tehran, Iran
jjavadpour@mail.iust.ac.ir

M. Hosseinzadeh

Par Refractories Co., Yazd, Iran
Pars.ref@mail.neda.net.ir

V. G. Marghussian

Department of Materials and Metallurgical Engineering
Iran University of Science and Technology, Tehran, Iran
marghussian@mail.iust.ac.ir

(Received: April 25, 2001 - Accepted in Final Form: April 29, 2002)

Abstract The present study was undertaken to improve the quality and increase the life time of magnesia-chromite refractory bricks used in the copper and lead industries. The results show that a decrease in the amount of large chromite particles in the formulation improves the thermomechanical properties and also reduces the slag penetration in the bricks. In addition, it was observed that the use of co-clinker decreases the open porosity in the bricks and thereby improves the mechanical properties. It was also shown that the use of around 4 percent iron oxide has beneficial effect on the bricks properties. Microstructural evaluation on the bricks shows increased formation of spinel phase and more direct bonding in the improved bricks.

Key Words Magnesia-Chromite, Particle Size Distribution, Chemical Composition, Slag Penetration, Spinel, Direct Bond

چکیده کار حاضر در جهت بهبود کیفیت و افزایش طول عمر آجرهای منیزیا-کرومیتی مصرفی درکنورترهای صنایع سرب و مس انجام یافته است. نتایج بدست آمده نشان می‌دهد که کاهش درصد کرومیت درشت دانـه در فرمولاسیون باعث بهبود خواص ترمومکانیکی و همچنین کاهش نفوذ سرباره در آجرها می‌گردد. همینطور ملاحظه گردید که استفاده از کلینکر منیزیا-کرومیتی و یا اکسید آهن در فرمولاسیون بدنه می‌تواند در کاهش درصد تخلخل در ریزساختار و بهبود خواص مکانیکی بسیار مفید باشد. بررسیهای ریزساختاری نشان میدهد که در آجـرهای بـا خواص بهتر، تشکیل فاز اسپینلی و پیوند مستقیم بین دانه افزایش یافته است.

1. INTRODUCTION

Due to high resistance of the magnesia-chromite bricks to the thermal shock and against the basic slag attack, these bricks are used extensively in the production of ferrous and non-ferrous metals industries [1]. Among the more important application of this type of bricks is their use in the Pierce Smith (P.S.) and Top Blowing Rotary (T.B.R) convertors in the copper and lead industries. Due to converter rotation, gas flow and repeated loading and unloading operations, the bricks are under thermal and mechanical stresses [2-3]. Therefore, the bricks used for this purpose must possess good thermal shock resistance, low slag

TABLE 1. The Chemical Analysis of the Raw Materials.

Raw material \ Oxide (wt%)	MgO	Cr_2O_3	SiO_2	CaO	Al_2O_3	Fe_2O_3
Imported Magnesia	96.93	--	0.66	1.86	--	--
Chromite	20.60	34.18	2.82	--	27.48	12.75
Co-clinker	68.31	12.51	2.74	1.12	9.55	5.09
Iron-oxide	--	--	Trace	--	--	99.9

penetration with good high temperature mechanical properties [4]. Previous work in this area has shown that direct bonding and formation of a spinel phase within the magnesia grains and along the grain boundaries, are very influential parameters in improving the bricks properties [5]. Therefore, in order to improve the properties of the bricks produced by Pars Refractory Manufacturing Co. (Iran), it was decided to carry out a more detailed study on the effect of processing parameters on the microstructure and properties of the magnesia-chromite bricks used in copper and lead industries.

2. EXPERIMENTAL PROCEDURES

The main raw materials used in this investigation were imported dead-burned magnesia, and a domestic type of chromite. The co-clinker material added to the body formulation was from the rejected bricks fired at 1650°C. The chemical analysis of the materials used in this investigation are given in Table 1.

Pressing of the formulated bodies was performed at 1100 kgf/cm^2 and the pressed samples were fired at 1650°C for 4 hrs. Dimensions of the samples were 400×160×140×100mm (thickness varies) after firing. Bulk density (BD), Modulus of rupture (MOR), hot Modulus of rupture (HMOR), slag penetration and thermal shock resistance (TSR) of the fired samples were evaluated.

The latter parameter was evaluated by comparing the MOR values before and after the thermal shock experiments. This test involved taking the sample from RT up to 1000°C and measuring the MOR values in the air quenched samples. The bulk density of the samples was measured using Archimedes technique. The slag penetration depth in the samples was taken as a measure of corrosion resistance.

The microstructural details of the specimens were studied using optical microscope, SEM/EDS and XRD. All the tests performed in this work were according to JIS standards.

3. RESULTS AND DISCUSSION

Effects of the processing parameters on the properties of the magnesia-chromite bricks were studied in the following manner:

3.1 Effect of Chromite Particle Size Distribution Figure 1 shows the effect of coarse chromite particles (1-4mm) amount on the open porosity in the bricks. An increase in the amount of coarse chromite particles causes the open porosity in the microstructure to increase significantly. It is believed that the observed behavior is the result of thermal expansion mismatch between the chromite

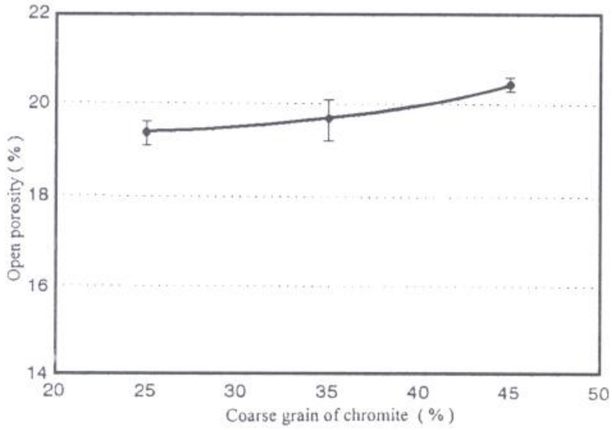


Figure 1. The effect of chromite size on the open porosity in the magnesia-chromite bricks.

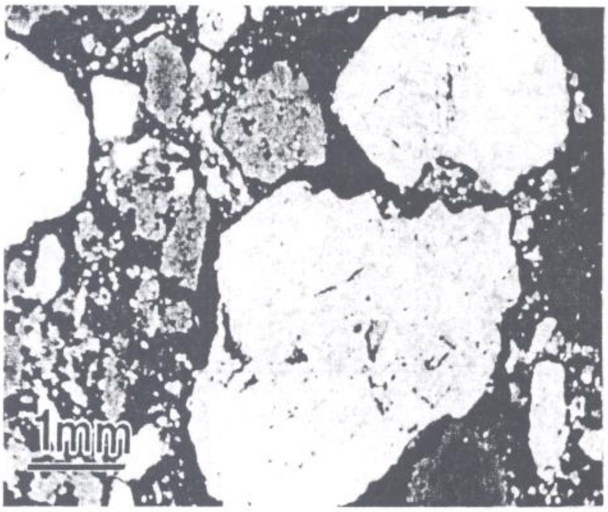


Figure 2. The formation of gap around the chromite particles. Magnesia: gray phase; Chromite: light phase; gaps: dark areas.

particles and the matrix which leads to the formation of gaps in the microstructure during the cooling process [4]. The larger the percentage of the particles the larger the gap would be (Figure 2).

The increase in the open porosity has a degrading effect on the cold crushing strength (CCS) & hot modulus of rupture (HMOR) values in the bricks (Figure 3).

On the other hand, an increase in the open porosity, i. e. an increase in coarse chromite particles has a positive effect on the thermal

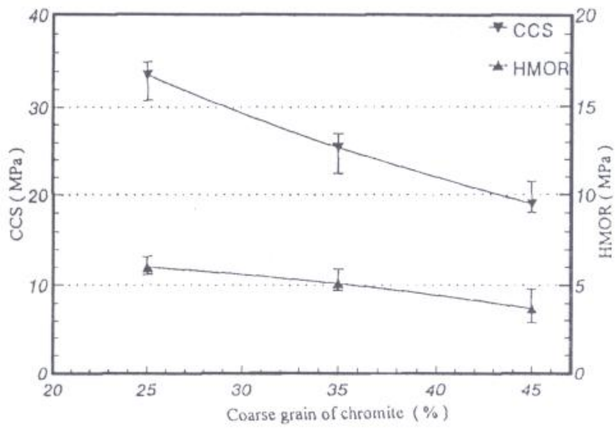


Figure 3. The effect of large chromite particles amount on CCS and HMOR values at 1000°C.

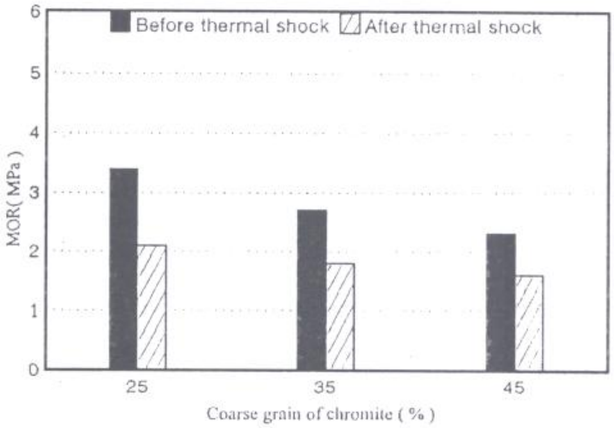


Figure 4. The effect of coarse chromite particles amount on the MOR values after thermal shock cycles.

shock resistance. The conclusion is made by comparing the MOR values before and after thermal shock treatments as presented in Figure 4.

Apparently the gaps around the chromite particles act as a barrier to crack growth [4]. In order to study the effect of chromite size on the corrosion resistance, the Cu-slag penetration test was conducted. This crucible test was carried out at 1450°C for 5hrs in a reducing atmosphere. The corroded samples were evaluated as to the extent of penetration using optical microscopy. The results (Figure 5) show that the penetration is deeper in samples with

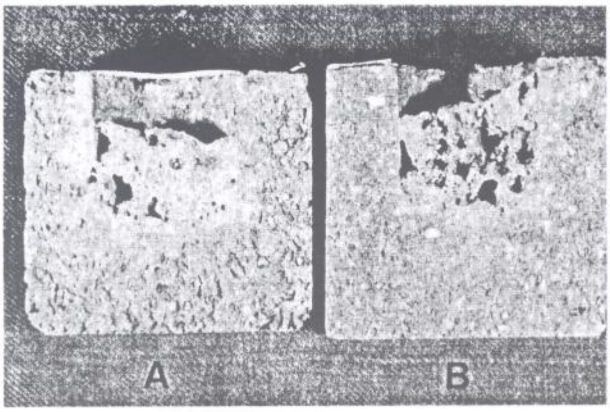


Figure 5. The effect of chromite particle size on Cu-slag penetration depth. sample with higher (A) and lower (B) percentage of coarse grains.

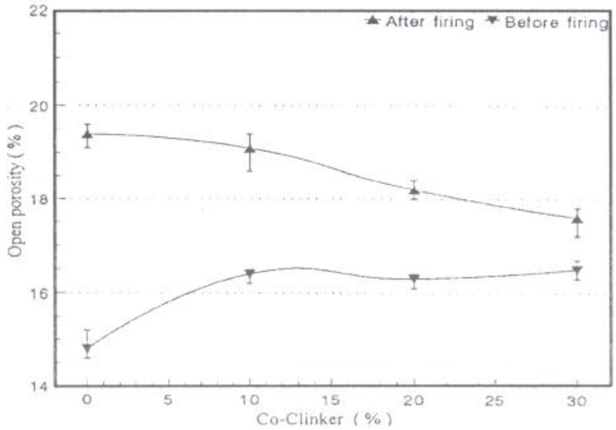


Figure 6. The effect of co-clinker addition on the open porosity in the bricks.

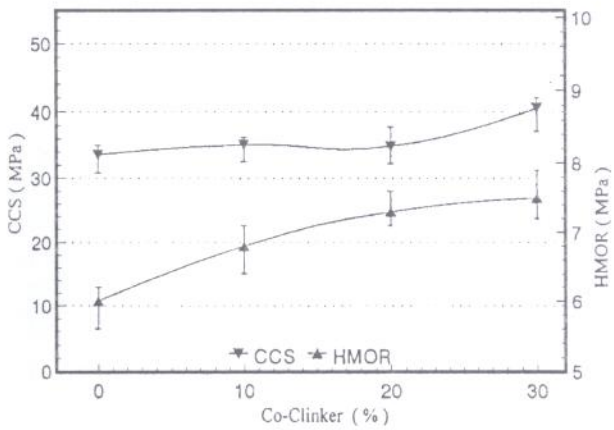


Figure 7. The effect of co-clinker addition on CCS and HMOR values at 1000°C.

higher percentage of coarse grained chromite particles.

3.2 The Effect of Using Magnesia-Chromite Co-Clinker Figure 6 presents the effect of co-clinker addition to the amount of open porosity in green and fired bricks. It can be seen that in the green state, the open porosity increases with the increase in the co-clinker content. This is partly due to the presence of porosity within the co-clinker particles. It is also observed that in the fired samples, porosity decreases as the amount of co-clinker material increases. The cause of this behavior is believed to be the presence of silicate phases accompanying co-clinker particles, which provide better sintering and reduce porosity in the samples.

The effect of co-clinker addition on CCS and HMOR values are shown in Figure 7. Both the CCS and HMOR values at 1000°C showed improvement using co-clinker particles. To explain these results, it should be reminded that sintering results in contraction between magnesia grains whereas the same process causes expansion in magnesia and chromite particles due to the formation of secondary spinel phases [6-8]. Replacing magnesia powder by co-clinker reduces the expansion reactions and related stresses in the microstructure. The other possible reason for the improved mechanical strength can be related to the improved densification in the presence of silicate phases [8-9].

3.3. The Effect of Iron-Oxide Addition The use of iron oxide resulted in a decrease in the open porosity of the samples (Figure 8).

In order to explain this behavior it should be noted that the solubility limit of iron oxide in magnesia lattice is much more than those of Al_2O_3 and Cr_2O_3 [1]. In fact, the solubility of

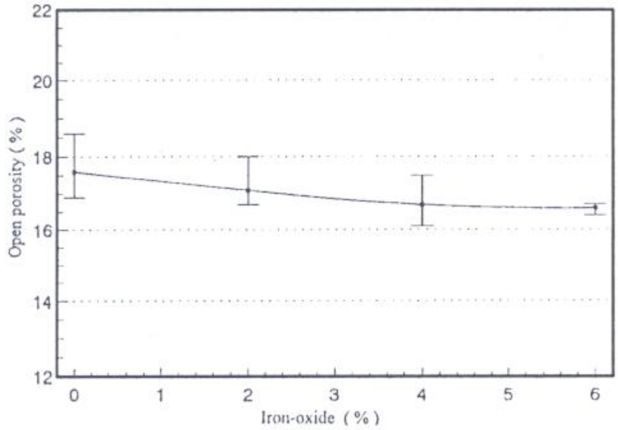


Figure 8. The effect of iron-oxide addition on the open porosity in the bricks.

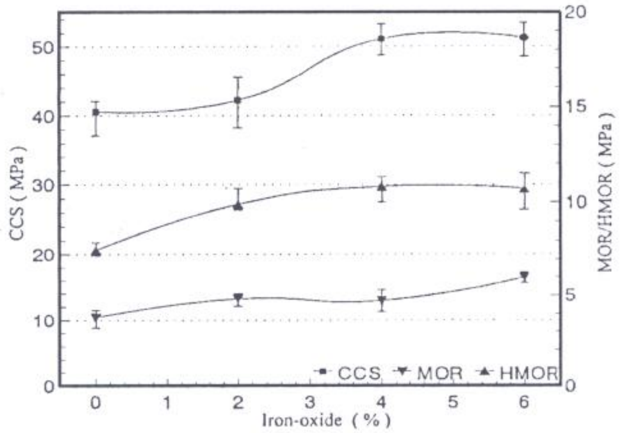


Figure 9. The effect of iron oxide addition on the CCS, MOR and HMOR values of the bricks.

iron oxide increases with an increase in the temperature and around 1800°C, the solubility becomes unlimited [7-10]. Therefore upon heating, iron oxide enters the magnesia lattice, creating cation vacancies according to the following reaction:

$$Fe_2O_3 \rightarrow 3O_O + 2Fe^{\circ}_{Mg} + V''_{Mg}$$

Vacancies produced in this manner, increase the diffusion rate and provide better connection between adjacent grains which in turn reduce

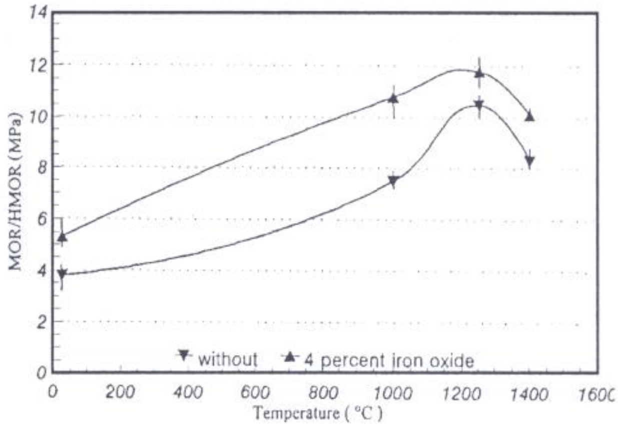


Figure 10. MOR & HMOR values in the bricks containing 0.4 percent iron oxide.

the open porosity in the samples [10-11]. Figure 9 also shows that the use of iron oxide helps in improving CCS, MOR and HMOR values in the bricks.

This can be related to the improved densification and more direct bonding in the samples containing iron oxide [10].

In Figure 10, MOR values for the magnesia-chromite bricks have been presented from RT up to 1400°C.

It is observed that by increasing the temperature, the MOR values of the bricks also increase. This behavior in the magnesia-chromite bricks is due to thermal expansion mismatch stress release which occurs with the rise in the temperature [12]. Starting at a temperature of around 1250°C, softening of the low melting point phases causes a decrease in the HMOR values [10,12]. It is also shown that the samples containing 4-percent iron oxide show better strength values, when compared with samples without any addition of iron oxide. Also the slag penetration in the samples containing 4-percent iron-oxide is much less in comparison with the samples without iron oxide addition (compare Figure 11a, 11b). This is due to the decreased open porosity in the latter samples.

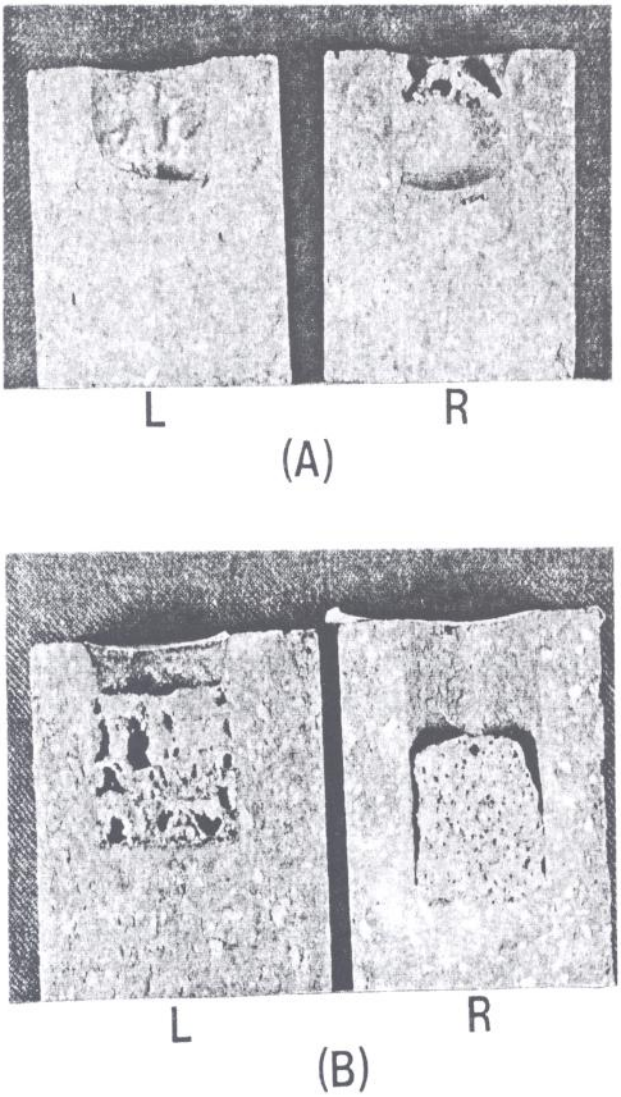


Figure 11. The effect of iron oxide addition on the slag penetration in the magnesia-chromite bricks. With (left) and without (right) iron oxide addition (A) Pb-slag and (B) Cu-slag.

3.4. Microstructural Investigations Figures 12 and 13 show SEM micrographs of samples containing iron oxide. With iron oxide addition, there is a considerable increase in the amount of secondary spinel phases at grain boundaries and within the magnesia grains, which results in more direct bonding between particles in the microstructure.

The microstructural results obtained in this study agrees well with previous work [10]. The

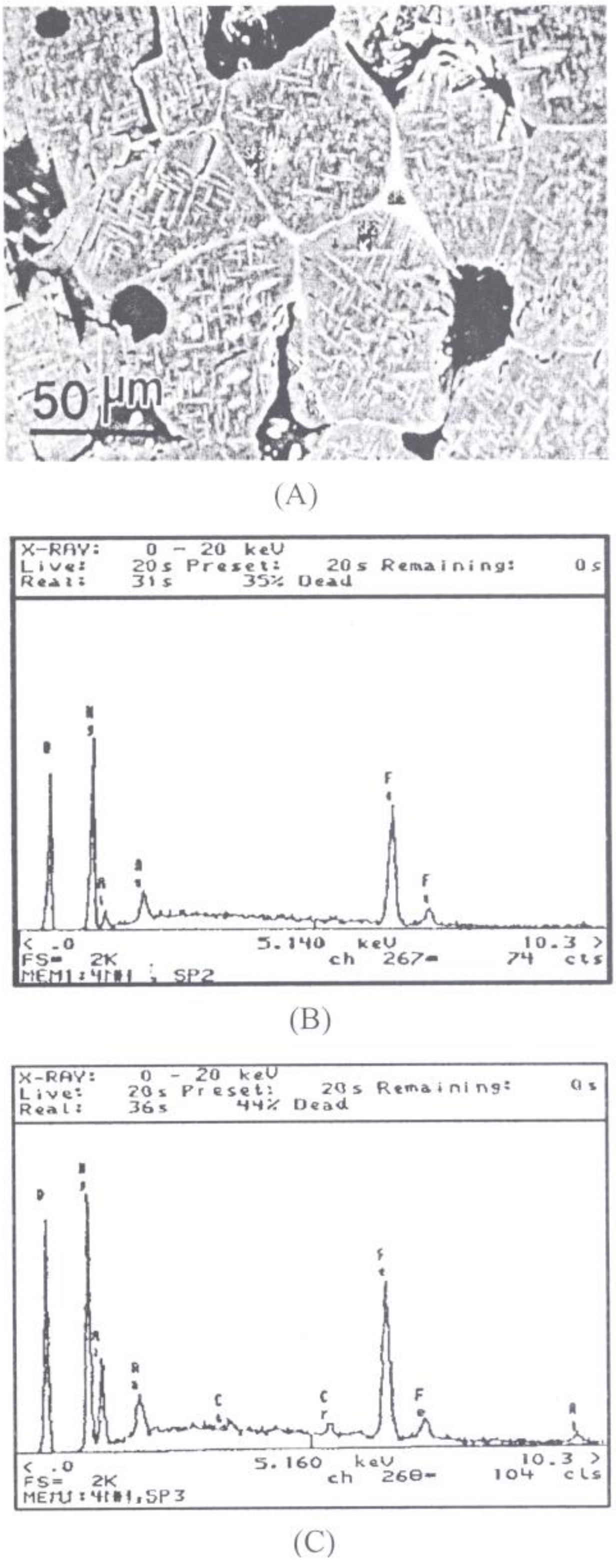
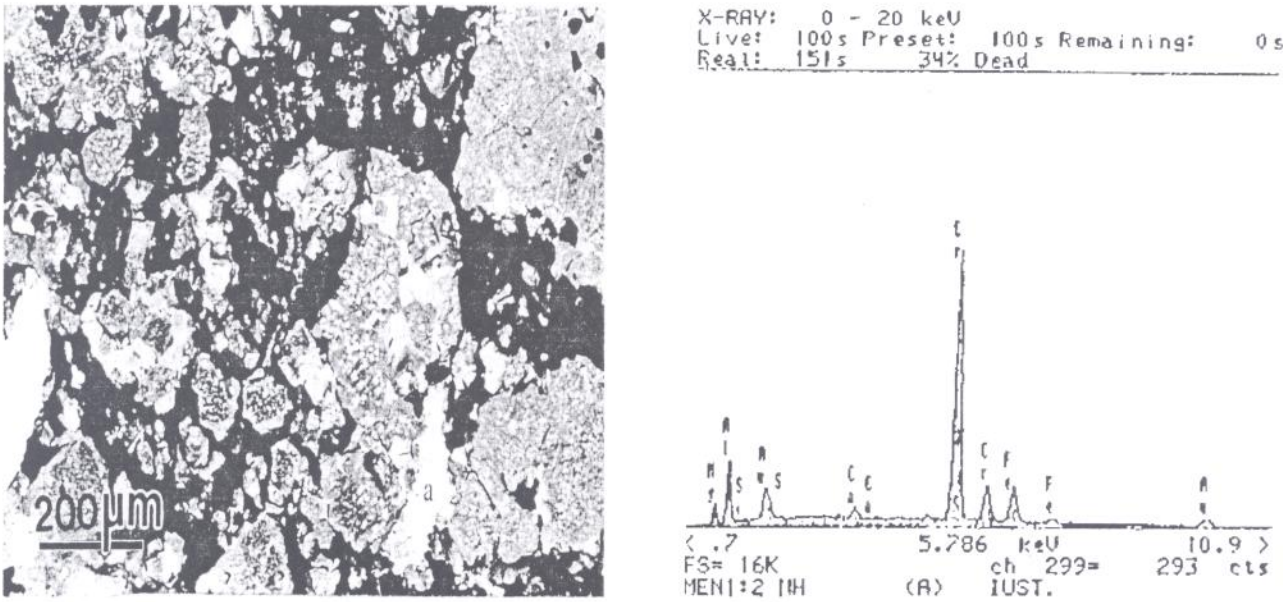


Figure 12. (A) SEM image from a sample containing 4-percent iron oxide, (B) EDS analysis taken from the point designated as Sp2 and (C) EDS analysis taken from the point designated as Sp3.



(A) (B)

Figure 13. (A) SEM image from a sample containing 4-percent iron oxide and (B) EDS analysis from chromite phase.

TABLE 2. Chemical Analysis of Regular and Improved Magnesia-Chromite Bricks.

Oxide (wt%) / Products	MgO	Cr_2O_3	SiO_2	CaO	Al_2O_3	Fe_2O_3
Regular	60.32	17.5	1.7	1.7	12.2	6.2
Improved Brick	57.6	16.9	2.4	1.6	11.6	9.8

TABLE 3. Physical and Mechanical Properties of the Regular and Improved Bricks.

Property / Products	AP (%)	BD (g/cm^3)	CCS (MPa)	MOR (MPa)	HMOR at 1000°C (MPa)	HMOR at 1400°C (MPa)
Regular brick	18	2.95	43	38	75	83
Improved brick	16.5	3.05	61	53	108	101

XRD patterns from the samples show the formation of magnesia-ferrite phase in the samples containing iron-oxide. EDS analysis from the phases present within the magnesia grains show a solid solution consisting of iron-oxide, magnesia, chromium oxide and some Al_2O_3.

Since the wettability of spinal phases by the molten salg is not as much as that of periclase, their formation in the microstructure improves the corrosion resistance of the bricks [5,14,15]. Tables 2 and 3 compare the chemical, physical and thermomechanical properties of regular and improved bricks.

4. CONCLUSIONS

1. It was concluded that the processing parameters such as chromite particle size, use of co-clinker and iron-oxide in the body formulation have a beneficial effect on the brick properties.
2. With decreasing the amount of the coarse chromite particles, improvement both in the corrosion resistance and thermomechanical properties of the bricks was observed.
3. The use of magnesia-chromite co-clinker reduces the open porosity in the bricks, thus improving their mechanical properties.
4. The use of up to 4-percent iron-oxide gives greater resistance against slag penetration, thus improving high temperature mechanical properties of the bricks.
5. The use of magnesia-chromite co-clinker and iron oxide encourages the formation of secondary spinel phase and more direct bonding in the microstructure.

5. ACKNOWLEDGEMENT

The authors would like to thank Mr. S. Roshanfekr, the managing director of Pars Refractories Co., for his full technical and financial support throughout the project.

5. REFERENCES

1. Kim, C., Kohler, A. and Warner, L., "Chrome in Refractories", ***Ceramic Industry***, (Sept. 1992), 57-61.
2. "Stress of Ankrom-S55 Bricks in a Pb-Zn-Kaldo Converter, NILZ, IRI", Forschungsinstitut Leoben, Technical Report, (1998).
3. "Specific Wear Parameter for MgO-Based Refractory Material in the Lead Producing Industry", Veistscher, Technical Report, Vienna, March (1998).
4. Tamaki, K., Yoshitomi, T., Andou, H. and Yamato, T., "Improvement of the Structural Spalling Resistance of Magnesia Chromite Bricks", ***Taikabutsu Overseas***, Vol. 19, No. 4, (1999), 30-34.
5. "Refractory Technology in the Copper and Nickel Industry", V. Fishter Technical Report, Dec (1969).
6. Hyuga, H., "Shortage of Cold Crushing Strength", Minoyogyo Co., Technical Report, (1995).
7. White, J., "Magnesia Based Refractories", in High Temperature Oxide-I, Edited by A. M. Alper, Academic press, New York and London, (1970), 77-139.
8. "Properties of Refractories", in Modern Refractory Practice, Edited by J. P. Sutton and S. W. Thrower, Harbison-Walker Refractories, USA, (1992), 1-32.
9. Bundnikov, P., "Spinel Refractories and Their Combination With Magnesite", in the Technology of Ceramics and Refractories, Massachusetts Institute of Technology, USA, (1964), 283-295.
10. Chose, R. K. and White, J., "Constitutional Factors Affecting the Relationship between CaO/SiO_2 Ratio and Hot Strength in Magnesia-Based Refractories", ***Transaction Journal of the British Ceramic Society***, Vol. 79, (1980), 146-153.
11. Kriek, H. J. S., Ford, W. F. and White, J., "The Effect of Additions on the Sintering and Dead-Burning of Magnesia", ***Transaction Journal of the British Ceramic Society***, Vol. 55, (1956), 1-26.
12. Claraud, B., "Hot Mechanical Properties of Refractories-Compressive Strength", ***Transaction Journal of the British Ceramic Society***, Vol. 74, (1975), 113-119.
13. Ikesuel, A., et al., "Formation of Precipitated-Complex Spinel in Magnesia-Chrome Refractories and its Characteristics", ***Interceram***, Vol. 41, No. 6, (1992), 406-409.
14. Riepl, K. and Barthel, H., "Large Crystal Magnesia Clinker for Advanced Refractories, an Update and Overview", ***Unitecr 91 Congress***, Aachen, Germaney, (1991), 66-69.
15. Barthel, H., "The Use of Magnesia Chromite Refractories Made from Sintered Co-clinker in Secondary Steel Making and Open Hearth Furnaces", ***Proceeding of the International Symposium on Refractories Hangzhou*** China, (1988), 489-504.