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FELLOWSHIP FINAL REPORT

Improvement of methods to determine key properties related to the corrosion behaviour of refractories

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REPORT INFO

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ABSTRACT

The project aims to contribute to the improvement of methods for determining key properties in the evolution of gas and liquid corrosion of refractory products. In particular, the project proposes to develop in-lab methods to measure transport properties at high temperature, specifically, the intrinsic permeability and the capillary suction properties, which are not available in the present time. As the first step, a deeper comprehension of the factors controlling the materials' transport properties at room temperature, such as the porosity characteristics, are required in order to advance to the adaptation of the methodologies for measuring the properties under high temperature conditions. The tasks carried out during the staying at CEMHTI were aligned with the original plan and will continue during the following months to achieve the proposed aims. Non-commercial as-received and heat-treated MgO-C refractories, previously studied at INTEMA, were tested. On the other hand, the high temperature properties of molten steelmaking slags were measured using the aerodynamic levitation technique. In addition, a new thermodynamic simulation model to study the graphite oxidation of oxide-C refractories was also developed and applied.

1- Introduction

A material is defined as *refractory* when it has the ability to withstand high temperatures without decomposing, degrading or altering in a significant way. This characteristic makes refractory ceramic materials (hereinafter referred to as 'refractory materials' or 'refractories') an indispensable input for various basic industries, such as cement, petrochemical, glass and metallurgical industries. However, the stability of these materials can be compromised due to extremely demanding service conditions, including fluid and particle movements, corrosive atmospheres, severe mechanical stresses and high temperatures. Chemical wear, known as 'corrosion', is caused by thermodynamic incompatibility between an external agent and the refractory material, and in many situations is the process which limits the refractory lifetime.

In particular, *gaseous corrosion* is considered as the chemical degradation of refractory materials due to their interaction with the surrounding gases, usually at elevated temperature. It is a complex process, which will depend on the type of refractory, as well as on the atmosphere composition and temperature prevailing in the industrial process. Consequently, also the effects of the gas-refractory interaction on the material characteristics and properties are diverse, and impact to different degrees on the materials' performance in service. In this field, air and water vapour have been among the most studied corrosive species, in addition to some more specific agents, such as sulphurous gases in oxidic refractory materials or chlorine-containing gases in non-oxidic materials [1-6]. One of the cases that has generated most attention is the oxidation of graphite in an important materials family, i.e., C-oxide refractories [4, 7, 8].

The attack of refractory materials by melts (*liquid corrosion*), as in the case of gaseous corrosion, involves both chemical reactions and physical or mechanical phenomena, acting in parallel, synergistically; these processes depend, among other external factors, on temperature [9]. While most metals do not wet refractory materials, which is a necessary condition for corrosion to occur, liquid slags and glasses do. Dissolution of the refractory components occurs and chemical reactions are triggered from which more stable phases are formed. The solubility of solids in liquids and the kinetics of chemical reactions are strongly dependent on thermal conditions, and in general both processes are benefited by increasing temperature. Generally, the gases escape, or dissolve in the melt, while the liquids and solids may remain at the reaction interface, forming a layer that could hinder the progress of corrosion (depending on its stability). There are many and varied melt-refractory systems which have been studied, and they continue to be a topic of great interest in both the industry and the academia, with very recent examples of articles of acid [10], basic [11] and C-oxide [12] refractories.

In addition to thermodynamic incompatibility, there are other factors to be considered in the development of the corrosion process, whether gaseous or liquid. Although the first contact between the reactive agent and the refractory is through its external surface, the former will subsequently enter inside the solid through its open pores and microcracks, and corrosion will continue. The physical property that commonly characterises the ability of a solid to allow a fluid to penetrate it is the *intrinsic permeability*. In the case of refractory materials, the permeability is currently measured at room temperature using a gas under steady state conditions [13, 14] (although a liquid could be also used as fluid). However, there are some issues regarding the experimental conditions and the modelling of the process to obtain an accurate value of the property which have demanded more attention [15]. Moreover, an ongoing challenge in the field of refractory materials is to measure permeability at high temperature.

Nevertheless, this property does not describe the fluid-refractory interactions completely. The corrosion could be described as a 'reactive transport process', since chemical reactions take place as the fluid moves inside the solid. Ideally, fluid transport and chemical reactions should be addressed separately before coupling them. One of the transport properties of the refractory is the intrinsic permeability, and the other one is the *capillary suction property*. Even little attention has been paid to this last property of refractories, it has been measured by a dedicated capillary rising test at room temperature using glycerine as the non-reactive fluid [16, 17]. On the other hand, no attempt to measure this property at high temperature has been reported until now. The surface tension of the liquid and its viscosity strongly affect the interaction degree with the solid. I turn, these properties are conditioned by the composition of the melt and the temperature.

The proposed project aims to contribute to the improvement of methods for determining key properties in the evolution of gas and liquid corrosion of refractory products. The achievement of this goal will allow a better and deeper understanding of the phenomena involved, in order to achieve the control of corrosion, which in many cases limits the material lifetime.

In order to achieve this general objective, the following specific objectives are proposed for the stay at CEMHTI:

-To adapt and apply the methodologies currently in use for the determination of transport properties in as-received, tested and/or heat-treated refractory materials, at room temperature.

-To advance in the design of tests (equipment, experimental protocol, modelling and data processing) for determining the transport properties at high temperature based on the one currently in used for cold measurements.

-To determine high-temperature properties of steelmaking slags (viscosity, surface tension and density) by the aerodynamic levitation technique (ADL), including the required modifications.

2- Experimental details

Materials

Non-commercial MgO-C refractory bricks, with known and controlled compositions, prepared with the technology used in the plant, were evaluated. A set of 8 materials (Table I) were formulated with differences in the amount of graphite and antioxidant, and the type of organic binder. They were extensively studied (at INTEMA) in relation to their characteristics, mechanical behaviour, gas and slag corrosion, and thermal shock response.

Table I: Composition and label of MgO-bricks.

Brick	Binder(1)	Magnesia (%wt)	Graphite (%wt)	Antioxidant(3) (%wt)
R8-0	Phenolic resin	89	8	0
R8-A		87		2
R12-0		85	12	0
R12-A		83		2
SB8-0	Phenolic resin + Ecobinder(2)	89	8	0
SB8-A		87		2
SB12-0		85	12	0
SB12-A		83		2

(1)3 wt.% (2)Modified pitch (3)Aluminium

Moreover, the high temperature properties of industrial steelmaking ladle slags containing mostly CaO, Al_2O_3, SiO_2 and MgO, and different FeO/Fe_2O_3 contents were evaluated.

Experimental techniques

The gas intrinsic permeability (at room temperature) of samples (35 mm in diameter and 40-50 mm in height) of the as-received MgO-C bricks, prepared by cutting at CEMHTI, were evaluated. The permeameter developed by the CEMHTI [15] was used, with N_2 as flowing gas (1.7 NL/min), in atmospheric mode (AM). In this mode, either the flow rate or the inlet pressure is set and the exit remains at atmospheric pressure. In addition, heat-treated samples were tested in the same equipment and conditions. For the treatment, a low temperature was selected in order to favour the organic binder pyrolysis but minimising the oxidation of graphite. The sample was then introduced in a graphite bed, using a tubular furnace (Nabertherm) and the following schedule: heating up to 500°C (10°C/min), permanence of 5 h, and free cooling.

The texture of as-received MgO-C materials was also characterized. The pore size distribution < 1 mm was evaluated by Hg-porosimetetry (Micromeritics, AutoPore IV 9500 V1.10). Furthermore, the global density and apparent porosity were determined by the Archimedes method using isopropanol as the liquid medium.

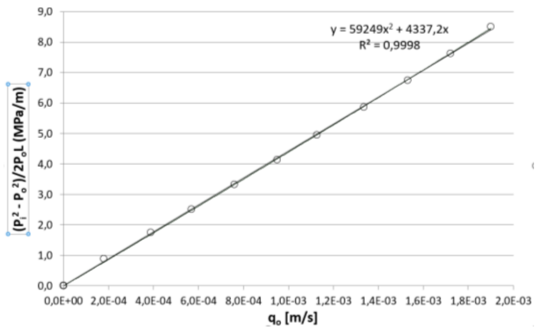
The melting temperature and thermophysical properties such as viscosity, surface tension and density of the two industrial steelmaking slags were determined by the ADL technique available at CEMHTI [18, 19]. The measures were performed in two atmospheres: 100 % Ar and a mixture of 100 % Ar and 20 % O_2

Thermodynamic simulation

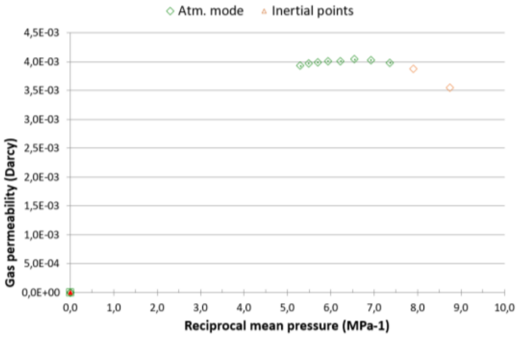
As a contribution to the study of refractory gaseous corrosion, a new iterative model to simulate the graphite oxidation of oxide-C refractories was developed using the commercial software FactSage V.8.2 available at CEMHTI. The oxidation behaviour of the set of eight MgO-C bricks and four additional Al_2O_3-MgO-C (AMC) materials previously studied at INTEMA, was analysed using this thermodynamic approach. The equilibrium phases present in the refractories between 700 and 1400°C in oxidant atmosphere were calculated.

3- Results and discussion

Typical Darcy and Klinkenberg plots obtained during the permeability test of MgO-C samples are shown as example in Figure 1. With the exception of one sample (R8-0), the rest of materials could be properly measured, in spite of their relatively low porosity. The raw data still need to be carefully revised in order to keep with those values obtained in the proper experimental conditions (viscous gas flow). Although this analysis has not been done yet, some tendencies observed in a first sight will be mentioned here. An almost linear Darcy plot (Figure 1(a)) was obtained for the tested materials, which means that there are not inertial effects during the measurements. On the other hand, if the first points in the Klinkenberg plots are dismissed (the red points in Figure 1(b)), insofar as they manifest a positive tendency as pressure increases indicative of gas diffusion (instead of viscous flow of the gas, necessary to a proper measurement), a null or slightly negative slope was determined for every refractory. A zero slope means that the permeability is determined by large pores. Even the raw data need a further analysis, an estimation of the intrinsic permeability was obtained, and the values are reported in Table II for the set of as-received MgO-C refractories.



(a)



(b)

Figure 1. Darcy plot (a) and Klinkenberg plot (b) of as-received R12-0.

During the stay at CEMHTI, only three refractories (R12-0, SB12-0 and SB8-0) were thermally treated, and also tested in the permeameter. After the treatment, the samples only lost a percentage of mass lower than around 1 wt.% and accordingly, the intrinsic permeability seems to decrease slightly. These results suggest that organic binder effectively pyrolysed during the treatment and new carbon from the Boudouard reaction (2 CO → ½ O2 + 2 C) would block the pores. This reaction could be favoured by the oxidation of the graphite forming the bed. This hypothesis will be This hypothesis will be tested once the treatments and experiments for all the materials are completed. Moreover, Raman spectroscopy at high temperature will be performed in order to obtain more information about the thermal evolution of the systems.

The apparent porosity of the as-received MgO-C samples determined at CEMHTI is also reported in Table II. At a first sight, the estimated intrinsic permeability does not correlate well with the volume of open pores.

Table II: Intrinsic permeability (*Kp*) and apparent porosity (π_A) of as-received MgO-bricks.

Brick	*Kp* (mD)	π_A (%)
R8-0	-	2.5 ± 0.4
R8-A	0.6	4.1 ± 0.6
R12-0	3.4	4.1 ± 0.2
R12-A	1.7	3.6 ± 0.2
SB8-0	0.9	6.4 ± 0.7

SB8-A	0.9	3.0 ± 0.3
SB12-0	4.5	4.9 ± 0.2
SB12-A	2.5	5 ± 1

Figure 2 shows the differential pore size distribution curves for the four tested samples of as-received R12-0. The measurements were conducted for the complete set of materials, but the data were not analysed yet.

The measurement of the high temperature properties of the industrial molten slags by ADL was successfully performed in spite of their compositional complexity. However, the raw data obtained for high-Fe_2O_3 content slag were less accurate due to experimental drawbacks found during the runs. The data are now processing and will be further analysed.

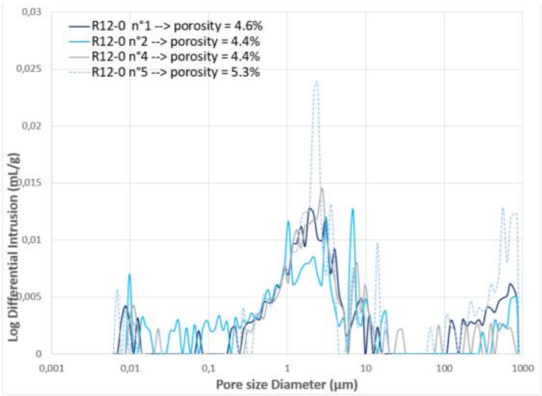


Figure 2. Differential curves of pore size distribution for as-received R12-0 samples.

4- Conclusion

The cooperative work conducted during the stay at CEMHTI was very fruitful and extended the scope of the collaboration.

Regarding the specific objective of the original project, the availability of samples of eight different MgO-C refractories opened the possibility of carrying out a deep study of the relationships between the intrinsic permeability and the characteristic of the material' porosity. For the moment, it seems that the apparent porosity is not the only factor determining the intrinsic permeability of the as-received materials. Moreover, the measurements conducted on some of the refractory samples showed that after a thermal treatment at 500°C under non-oxidant atmosphere, the intrinsic permeability slightly decreased. On the other hand, the high temperature measurement of the industrial steelmaking with different FeO/Fe_2O_3 contents were successfully carried out by ADL.

In order to achieve the general and particular objective of the project during the next months, both groups will continue working together in the planned activities.

5- Perspectives of future collaborations with the host laboratory

The proposal was planned as a long-term collaboration from the beginning. In view of the scope acquired by the study of transport properties of the materials under investigation, particularly the intrinsic permeability, and considering the progress achieved during the research stay at CEMHTI, many tasks, including experimental testing and data analyses will be conducted at CEMHTI and INTEMA in the next months. The specific goal of this part of the project is to understand the relationships between transportation properties and refractory's texture at room temperature for this special type of complex bricks. In the same framework, the heat treatments of samples will be completed, as well as the permeability and the textural characteristics evaluation. Other techniques such as *in-situ* XRD and Raman at high temperatures, available at CEMHTI, will be applied to understand the changes which take place during the staying at middle to high temperature range.

Both groups, from CEMHTI and INTEMA, will continue the discussion and interchange of ideas about the design of methodologies for measurement of transportation properties at high temperature. On the other hand, the collaboration will continue in the optimization of using the thermodynamic simulation for the study of the corrosion behaviour of refractories.

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Besides the specific tasks that should be conducted to achieve the proposed goals in each laboratory, and periodical virtual meetings, it has been planned to apply for economic help in order to cover the expenses of the exchange of people between both places.

6- Articles published in the framework of the fellowship

During the stay at CEMHTI, the following article reporting results of the thermodynamic simulation of oxide-C refractories was written and submitted:

*D. Gutiérrez-Campos, E. De Bilbao, A.G. Tomba Martinez, "Chemical degradation of steelmaking refractories – Revisiting the use of thermodynamic simulation as analysis tool", Special Issue *Thermodynamics for Sustainable Ceramics*, Journal of the American Ceramic Society.

Other papers will be written in the next future reporting the results of the on-going work for possible publication in high-impact scientific journals, as well as articles to be presented in scientific meeting.

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8- References

[1] D.W. Readey, Corrosion of ceramics in halogen-containing atmospheres, J. Eur. Ceram. Soc. 18 (1998) 2383.

[2] M. Fritsch, H. Klemm, M. Herrmann, B. Schenk, Corrosion of selected ceramic materials in hot gas environment, J. Eur. Ceram. Soc. 26 (2006) 3557.

[3] P. Prigent, M.L. Bouchetou, J. Poirier, Andalusite: An amazing refractory raw material with excellent corrosion resistance to sodium vapours, Ceram. Int. 37 (2011) 2287.

[4] A. Gerle, J. Podwórny, J. Wojsa, W. Zelik, High temperature gaseous corrosion resistance of MgO-containing refractories – A comparative study, Ceram. Int. 42 (2016) 15805–15810.

[5] M.K. Mahapatra, Review of corrosion of refractory in gaseous environment, Int. J. Appl. Ceram. Technol. 17 (2020) 606.

[6] A.Tixier, C. Varona, J.M. Brossard, P. Ganster, F. Valdivieso, J. Poirier, E. de Bilbao, Wear mechanism of oxide-bonded SiC refractory tiles in the combustion zone of waste-to-energy facilities, J. Eur. Ceram. Soc. 45 (2025) 117016.

[7] S.K. Sadrnezhaad, S. Mahshid, B. Hashemi, Z.A. Nemati, Oxidation mechanism of C in MgO-C refractory bricks, J. Am. Ceram. Soc. 89 (2006) 1308.

[8] M.N. Moliné, P.G. Galliano, A.G. Tomba Martinez, Chemical degradation of magnesia–carbon refractories by different gaseous atmospheres, Carbon Trends. 14 (2024) 100320.

[9] W.E. Lee, S. Zhang, Melt corrosion of oxide and oxide-carbon refractories, Int. Mater. Rev. 44 (1999) 11.

[10] S. Khanmohammadi, M. Mohtadinia, High temperature corrosion resistance of various aluminosilicate refractory bricks. Ceram. Int., 50 (2024), 49125.

[11] Q. Song, X. Zha, J. Shi, M. Gao, Y. Ma, Development of TiO2-doped MgO refractories with enhanced corrosion resistance for preparing high-purity nickel-based superalloys, J. Mater. Res. Technol. 35 (2025) 402.

[12] R. Zhang, Z. Liu, W. Qiu, S. Pan, W. Gu, L. Yuan, T. Wen, J. Yu, Corrosion mechanism of MgO–C refractories in V–Ti slag: Delve into the influence of ZrB2 additives, Ceram. Int. (2024). https://doi.org /10.1016/j.ceramint.2024.11.277.

[13] ISO 8884, Dense, Shaped Refractory Products–Determination of Permeability to Gases, 1991.

[14] ASTM C577-7, Standard Test Method for Permeability of Refractories, 2007.

[15] E. de Bilbao, L. Loison, Y. Hbiriq, C. Orgeur, S. Brassamin, T. Tonnesen, J. Poirier, Intrinsic permeability of refractories from gas permeability measurements: comparison of results. Ceram. Int. 44 (2018) 2900.

[16] E. de Bilbao, M. Dombrowski, N. Traon, T. Tonnesen, J. Poirier, E. Blond, Study of reactive impregnation and phase transformations during the corrosion of high alumina refractories by Al2O3-CaO slag, Adv. Mater. Sci. Technol. 92 (2014) 264.

[17] E. de Bilbao, J.Poirier, M. Dombrowski, Corrosion of high alumina refractories by Al2O3-CaO slag: thermodynamic and kinetic approaches. Metall. Res. Technol. 112 (2015) 607.

[18] E. Cheremisina, Z. Zhang, E. de Bilbao, J. Schenk, Density, viscosity and surface tension of high-silicate CaO–SiO2 and CaO–SiO2–Fe2O3 slags derived by aerodynamic levitation-The behavior of Fe3+ in high-silicate melts, Ceram. Int. 49 (2023) 4460.

[19] C. Denier, Z. Zhang, E. de Bilbao, J. Delacroix, P. Piluso, Thermophysical properties of liquid zirconia measured by aerodynamic levitation at high temperature, Int. J. Thermophys. 44 (2023)127.