

Dissolution of Magnesite and Dolomite in Simulated EAF Slags

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Abstract

Dolomite and magnesite are used as flux additions in EAF steelmaking for refining, refractory protection and developing a foaming slag. For these materials to perform these functions they must be in solution in the slag. In this study the mechanism and rates of solution of dolomite and magnesite were determined for EAF slag compositions using several techniques including SEM analysis and rotating cylinder dissolution. In contrast to oxygen steelmaking conditions, no solid calcium silicates were observed on the surface of the flux particles. Only solid $\text{FeO}\cdot\text{MgO}$ was formed on the surface of the magnesite. For similar conditions, the rates of dissolution of the two materials are similar. For magnesite the rate follows that predicted for liquid phase mass transfer control. For dolomite the mechanism is more complex. The CaO dissolves away and the MgO grains are released into the slag where they dissolve. For EAF conditions, the rates of dissolution of magnesite and dolomite will be approximately the same. If the basicity is less than two, the MgO content in the slag is below 6%, and the particle sizes are not excessively large both materials should go into solution easily. However, when the slag is nearly saturated with MgO , dissolution of magnesite will be slow.

Introduction

Fluxes such as lime (CaO), magnesite (MgO) and dolomite (CaO•MgO) are used in EAF steelmaking. The slag is designed to:

- Remove sulfur and phosphorus
- Reduce refractory wear and gunning
- Provide a forming slag for long arc operation

Refining for sulfur and phosphorus is favored by high basicity ($B = \% \text{CaO} / \% \text{SiO}_2$) and refractory wear is decreased with high basicity and MgO content. Foaming is best for slags with a $B = 1.5$ to 2.0 and FeO contents of 20 to 30%. In addition, for refractory protection and refining, the CaO and MgO must be dissolved in the slag. The solubility of MgO decreases from about 12 to 8% as basicity increases from 1.5 to 2.5, as shown in Figure 1⁽¹⁾. Excessive undissolved amounts of MgO in the slag could reduce refining and foaming. Once the CaO or MgO is in solution it does not matter from which material it originated.

It is therefore important to understand the rate of dissolution of flux materials such as lime, magnesite and dolomite. There has been a considerable amount of research on the dissolution of CaO for oxygen steelmaking (OSM) conditions. In OSM, FeO and SiO₂ in the slag react with solid CaO forming solid dicalcium silicate (2CaO•SiO₂). The temperature or FeO content of the slag must increase to dissolve the layer for further dissolution to occur. In the case of dolomite, in addition to 2CaO•SiO₂, a solid solution of FeO and MgO may also form. For MgO the solid phases discussed above can form along with 2MgO•SiO₂. The rates of solution may depend on the original porosity of the flux material. Of more importance in inhibiting dissolution is the nature and density of any solid product layers that form.

The rate of dissolution of these materials have been previously studied⁽²⁻⁵⁾. However most work was aimed at examining the behavior of refractories or fluxes in OSM. Refractory materials may behave differently than flux materials due to the fact they have binders and are fired at high temperatures. Also, the conditions in the EAF are considerably different than OSM. In the EAF the basicity is much lower, 1.5 to 2.0 compared to 3.0 to 4.5 in OSM. In the EAF, dissolution may proceed faster because $2\text{CaO}\cdot\text{SiO}_2$ is less likely to form on lime and dolomite, however $\text{MgO}\cdot\text{FeO}$ solid layer formation is still possible.

It is therefore the objective of this work to investigate the rate of dissolution of dolomite and MgO for EAF steelmaking conditions. The mechanism and rates were examined using several experimental techniques. The dissolution mechanism of dolomite used as flux material is of particular interest. Dolomite consists of a mixture of fine grains of MgO and CaO. If the CaO dissolves rapidly the MgO grains may simply fall off the dolomite and dissolve quickly because of their large surface area. Conversely if MgO dissolves quickly the CaO grains may go into the slag and dissolve.

Experimental

Three different types of experiments were conducted. In the dipping experiments the MgO or dolomite particles were submerged into the slag for a short period of time and withdrawn to determine the dissolution mechanism. In the other two types of experiments the rates of dissolution were determined. The chemical composition of the magnesite and dolomite used is given in Table 1.

Dipping Tests: Analytical reagent grade SiO_2 , CaO and Fe_3O_4 powders were dried and weighed to give a slag composition of 41.8%CaO-28.2% SiO_2 -30% Fe_xO . Approximately 50 grams of slag was contained in a magnesia crucible (46mm ID) and melted in a resistance

furnace. At 800°C the flushing gas was switched from Ar to a 50%CO-50%CO₂ gas mixture and held for four hours to reduce the Fe₃O₄ to Fe_xO. The slag was then heated to 1550°C. Particles of magnesite or dolomite, about 8 mm in diameter, contained in a molybdenum wire basket were dipped into the slag for 2 to 4 minutes and then withdrawn. The samples and the slag attached to their surface were mounted, polished and analyzed using a LX-FEG SEM. The final slag was analyzed and contained 37%CaO, 29.3%SiO₂, 25%FeO and 8.7% MgO.

In the experiments with dolomite the CaO dissolved first because initially the driving force for CaO dissolution was greater than for MgO. The slag picked up MgO from the crucible and its concentration was 8.7% which is close to saturation. The initial CaO content was 37%, much less than saturation. It is possible the opposite could be true depending on conditions. For example, if the MgO content of the slag is high and CaO is close to saturation it is feasible that the MgO will be leached away first and the CaO grains will erode into the slag. According to this reasoning the rate of dissolution of dolomite will be the rate for dissolution of CaO or MgO, depending on which is faster, with the other component going into the slag where it dissolves fairly fast due to the high surface area to volume ratio of the small grains.

Simple Dissolution: For studying the rate of dissolution, several types of crucibles were considered. Obviously MgO crucibles could not be used because they would dissolve increasing the MgO content of the slag. Alumina crucibles could not be used because the solubility of Al₂O₃ is too high, about 50% at 1550°C. The best choice was crucibles made of iron. The slag was prepared, as in the case of the dipping experiments and melted in a 32mm ID iron crucible. The experimental temperature was 1500°C. The additions consisted of 4 to 5 mm particles of magnesite (6.06 g), dolomite (12.16 g) or magnesite (5.31 g) plus lime (7.28 g). The MgO

addition in each case was about the same percentage of the slag weight. After the addition the samples of the slag were taken as a function of time.

Rotating Cylinder Experiments: In the dissolution experiments described above the surface area and mass transfer conditions were not clearly defined. Therefore, more controlled experiments using a rotating cylinder were conducted. A schematic diagram of the experimental equipment is shown in Figure (2). The equipment included a motor, which could be controlled from 50 to 500 rpm. About 150-175 grams of a slag containing about 40%CaO-30%SiO₂-30%FeO was contained in an iron crucible, which was heated to about 1500°C. The cylindrical samples were 10mm long by 7mm OD or 22mm by 12mm OD, had small holes (1.5-2.0 mm) for the rotation rod. The rod was made of iron. Iron discs were attached to both ends of the cylinders to stop dissolution from the ends. In the case of dolomite, due to difficulties in machining, the samples were first made from dolomite stone and then calcined at 1500°C prior to use. The samples were submerged into the molten slag and rotated at the desired speed for a predetermined time. The magnesite or dolomite samples were then withdrawn and a sample of the slag was taken. This procedure was then repeated with the same or a different sample. The rate was computed from the change in composition of the slag, which was in general agreement with composition computed from the change in diameter of the cylinder. The partially dissolved samples were examined using a SEM.

Results and Discussion

Dissolution Behavior

In the first series of tests, dolomite or magnesite particles were dipped into a synthetic EAF slag and withdrawn after 2 to 4 minutes and examined by SEM analysis to provide insight as to the

dissolution sequence or mechanism. There was a high degree of variability in the structure of the particles but some useful observations were made.

The materials tested were examined by SEM analysis prior to the reactions. The magnesia showed a clear grain structure with grains about 50-150 μm . A narrow boundary of SiO_2 , CaO and Al_2O_3 surrounded the grains. The dolomite showed no clear grain structure but a finely dispersed mixture of CaO and MgO .

Magnesite: For some of the magnesite particles as shown in Figure (3), slag penetrated into the particle and individual MgO grains were separated by slag, but the particle appeared to stay as one particle. In this case the interfacial area between solid MgO and liquid slag would increase significantly. For other particles, however, a distinct particle-slag interface was maintained with no sign of slag penetration.

Figure 4 shows, at higher magnification, the interface between the slag and MgO particles or grains. A thin (2 ~ 5 μm) layer of magnesiowustite was observed at the interface. Figure 5 shows the EDS spectrum of the MgO grain and boundary layer respectively. According to the EDS analysis the magnesiowustite consists of 39.5 mol% FeO -60.5mol% MgO . The melting point of this solid solution is about 1930°C. The formation of this solid layer on the surface of magnesia particle or MgO grains could impede the dissolution of MgO into the slag.

Dolomite: Unlike the case of magnesia, a distinct interface between the dolomite and liquid slag was always maintained without deep penetration of slag into the particle. This is shown by SEM images in Figure (6). Between the body of the particle and slag, there is a porous layer. It appears that in this layer CaO was “leached” away and MgO grains were left. Moving away from the interface towards the slag side, there is a layer (50 ~ 100 μm) in which MgO

grains were dispersed in the slag as shown in Figure (7). These particles will dissolve rapidly due to their high surface to volume ratio.

No magnesiowustite was observed surrounding the MgO grains. The reason for this is unclear. According to the EDS analysis, the molar ratio of CaO/SiO₂ in this slag is 1.48, higher than 1.1 in the case of magnesia. This is understandable considering that there is considerable amount of CaO in dolomite. At this high CaO/SiO₂ ratio, dicalcium silicate would precipitate from the slag which will make the slag highly viscous. This may explain why the slag could not fill the pores in the porous layer at the particle/slag interface in the case of dolomite. High viscosity of the slag will also deteriorate the mass transfer condition, which will impede the rate of MgO dissolution. Furthermore, as the CaO/SiO₂ increases due to CaO going into the slag the solubility of MgO in the slag will decrease. This will decrease the driving force for the MgO dissolution.

Simple Dissolution Experiments

In this section the results obtained for the dissolution rate of magnesite, magnesite plus lime and dolomite are discussed. The MgO and CaO contents of the slag were from chemical analysis and the amount of material dissolved was computed from the change in the analysis. The rate in terms of MgO content are shown in Figure (8). The rate of solution of MgO should not be compared to that for dolomite because in the case of dolomite CaO is also going into solution. With dolomite the basicity of the slag, (%CaO/SiO₂), increased from 1.34 to 1.65 as shown in Figure (9) which decreases the solubility of MgO from 13% to 8% and increases the melting point of the slag from 1455°C to 1510°C. When magnesite alone is added the basicity and the MgO solubility of the slag does not change.

Since in steelmaking, CaO is always added and needs to dissolve a more useful comparison is to compare dolomite to a mixture of magnesite and lime. This comparison is shown in Figures (8-10). In terms of magnesite, basicity and amount of material dissolved within the experimental scatter, the rates are virtually the same for MgO plus CaO and dolomite. These simple dissolution experiments indicate that for comparable conditions the rates of dissolution of a flux mix containing equal amounts of MgO and CaO and dolomite are similar. However, it is difficult to completely analyze the rates specifically because the mass transfer conditions are not defined. Furthermore, the slag composition, in particular the basicity increases, causing the MgO solubility to decrease which affects the driving force for dissolution to change.

Rotating Cylinder Experiments

Since the rate of dissolution may be controlled by mass transfer, the mass transfer conditions should be defined. For rotating cylinders they are defined but are not for the case of the simple dissolution experiments. Therefore, experiments were conducted for rotating cylinders and the conditions were such that the slag composition did not change significantly which would have changed the properties of the slag.

The dissolution of magnesite is less complex than dolomite. If the rate of dissolution is controlled by the rate of mass transfer, the flux equation for MgO (J_{MgO}) is given by (1):

$$J_{MgO} = m \left(C_{MgO}^S - C_{MgO} \right) \quad (1)$$

where

m = the mass transfer coefficient

C_{MgO}^S , C_{MgO} is the concentration of MgO at the surface and in the bulk slag.

Assuming that the concentration of MgO on the surface is the equilibrium solubility converting units to weight percent and integrating as a function of time the rate equation is given by (2)

$$\ell_n \frac{(\%MgO) - (\%MgO)_o}{(\%MgO)_e - (\%MgO)_o} = \frac{A \rho m}{W} t \quad (2)$$

where

$(\%MgO)$, $(\%MgO)_e$ and $(\%MgO)_o$ are the MgO content of the slag at time t, the equilibrium solubility and initial.

A is the surface area

ρ is the density of the slag

W is the weight of the slag

The area of the cylinder is changing with time, therefore equation (2) cannot be directly applied.

Equation (2) can be approximated by equation (3), where \bar{A} is the average area for that time interval.

$$\frac{W}{A \rho} \ell_n \frac{(\%MgO) - (\%MgO)_o}{(\%MgO)_e - (\%MgO)_o} = m t \quad (3)$$

The mass transfer coefficient for a rotating cylinder has been extensively studied. The most widely accepted correlation was developed by Eisenberg⁽⁶⁾ and is given by:

$$m = 0.0791 Re^{-0.3} Sc^{-0.66} V \quad (4)$$

where,

Sc = Schmidt Number γ/D

Re = Reynolds Number based on peripheral velocity of the cylinder (V)

γ = kinematic viscosity

D = Diffusivity of CaO or MgO in the slag

V = velocity of the cylinder surface

The results for MgO dissolution are plotted in Figure (11) in accordance with equation (3). The results give a reasonable straight line and the value of m computed from the slope is 4.2×10^{-4} cm/s. The use of equation (3) for computing the expected value of m depends on the values of diffusivity and kinematic viscosity. Using the values from the Slag Atlas⁽⁷⁾ of 4×10^{-5} (cm²/s) and 0.52 (cm²/s) respectively gives a value of 6×10^{-4} cm/s for m . Considering the uncertainties in the correlation and the values used, in particular the diffusivity, this agreement is considered reasonable. For example, if the diffusivity is 10^{-5} cm²/s the computed value of m is 2.5×10^{-5} cm/s. Also other researchers have proposed slightly different correlations. Therefore, within our knowledge of the mass transfer coefficient, the present results are consistent with mass transfer of MgO being the rate controlling mechanism.

Experiments were also run at 100 rpm. The rate should be slower than at 200 rpm. The mass transfer coefficient is approximately proportional to the rotation speed to the 0.7 power so that at half the rotation speed the rate should be about 35% slower when plotted according to equation (3). The rates slowed by about 25% which is in reasonable agreement with theory.

The case for dolomite is more complex. The CaO could dissolve rapidly allowing the MgO grains to fall into the slag as was the case in the dipping trials. Or the opposite could happen depending on the relative rates of dissolution of CaO and MgO. In the dipping tests the MgO content of the slag was relatively high (8.7%), since a MgO crucible was used, and the CaO content low (36.6%). Hence the driving force for the dissolution of CaO is high and dissolved first as expected. However, with the rotating cylinder experiments the concentration of MgO initially is low (<1%) and the driving force for dissolution of MgO is high and would be

expected to dissolve first. However, SEM analysis of the dolomite sample indicated the CaO was dissolving first; this was unexpected.

If the results for dolomite dissolution are analyzed using equation (3) which is for MgO dissolving first and controlling the rate the computed value of m at 100 rpm is 4.5×10^{-4} cm/s which is similar to what was observed for MgO dissolution. However, if CaO is dissolving first as observed using an equation similar to (3) but in terms of CaO the value of m is computed to be about 12×10^{-4} cm/s. The increased value of m is the results of a lower driving force. One might expect a solid calcium silicate to be on the surface or near the slag surface for CaO dissolution controlling the rate but it was not observed in this study.

Umakoshi et. al. ⁽³⁾ reported similar results. They used rotating cylinders and the rate of dissolution of dolomite and magnesite were similar. However, when the mass transfer coefficients for dolomite were computed based on CaO dissolving first they were about twice those for MgO. The absolute values of the mass transfer coefficients found by Umakoshi et. al. were similar to those found in this study.

Based on this study and previous studies the mechanism of dissolution of dolomite is not completely understood. When the CaO content of the slag is relatively low with respect to saturation with calcium silicate and MgO is close to saturation the CaO dissolves first allowing MgO grains to enter the slag where they dissolve. However, in cases when the MgO driving force is high the physical observation is that CaO still dissolves first. The reason for this is not fully understood at this time. This unexplained phenomena may be because the rate is affected and other factors such as the material losing mechanical strength and small grains simply are dislodged from the particle.

Industrial Application

The critical question is how well these materials behave in the EAF. In the EAF where the temperature is relatively high (1600°C) and basicity less than two, the CaO in the dolomite should dissolve rapidly and the MgO grains will enter the slag where they dissolve. Magnesite should also dissolve easily unless the slag is close to saturation with MgO. For example, at 1600°C and $\text{CaO/SiO}_2 = 2$ the solubility of MgO is about 9%. If the MgO content is close to this value the rate will be slow.

Crude calculations indicate that for EAF conditions, $T = 1600^\circ\text{C}$ and $B = 2$, dolomite particles that are not excessively large should dissolve easily. Magnesite particles should also dissolve easily if the MgO content is not close to saturation.

Conclusions

For MgO and CaO to be effective in EAF steelmaking they must be dissolved into the slag. The rate of dissolution and mechanisms of dissolution of dolomite and magnesite were examined in the study. The major conclusions are as follows:

- For dolomite, it appears that the CaO is dissolved away first and the MgO grains enter the slag where they dissolve. No solid layers of calcium silicate were found for EAF conditions.
- For magnesite, the slag penetrates into the particle and solid layers of $\text{FeO}\cdot\text{MgO}$ form on the MgO grains.
- The rate of dissolution of magnesite and dolomite are essentially the same for similar conditions.
- For rotating cylinders, the rate of dissolution of magnesite appears to be controlled by liquid mass transfer.

- For rotating cylinders of dolomite the rate in terms of mass dissolved per unit time is slightly faster than for magnesite.

- One unanswered question is that for all cases with dolomite the CaO dissolves first even though theoretically for mass transfer control in some cases MgO should dissolve first.

- For EAF conditions and the particle sizes of magnesite and dolomite commonly used the rate of dissolution of both materials are essentially the same. As long as the basicity is below about two, dolomite should go into solution rapidly. For magnesite the MgO content must also be significantly below saturation for rapid dissolution.

Table 1

Chemical composition (weight percent) of magnesite and dolomite studied

| | MgO | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ |
|-----------|------------|------------|------------------------|------------------------------------|------------------------------------|
| Magnesite | 93.5 | 1.7 | 3.0 | 0.5 | 1.3 |
| Dolomite | 40.8 | 57.2 | 0.2 | 0.1 | 0.1 |

References

1. Making Shaping and Treating of Steel, Steelmaking and Refining, Editor R. J. Fruehan, AISE, Pittsburgh 1999.
2. P. Williams, M. Suderland and G. Briggs, Ironmaking and Steelmaking, Vol. 9, 1982, pp. 150-62
3. M. Umakoshi, K. Mori and Y. Kawai, Second International Symposium on Slags and Fluxes, Reno Nevada, TMS, Warrendale PA, 1984.
4. F. Oeters and Y. Wannabe, Arch Eisenhuttenus, Vol. 50, 1979, pp. 37-42.
5. S. Kienow, R. Knuppel and F. Oeters, Arch Eisenhuttenwes, Vol. 46, 1975, pp. 57-64.
6. M. Eisenberg, C. W. Tobias and C. R. Wilke, Chem. Eng. Prog. Symposium Series No. 16, Vol. 51, 1955, pp. 1-16.
7. Slag Atlas, 2nd Edition, 1995, Stahl Eisen

Figure Captions

- Figure 1. The solubility of MgO in CaO-SiO₂-FeO slags. ⁽¹⁾
- Figure 2. Schematic diagram of rotating cylinder experimental equipment.
- Figure 3. SEM picture of magnesite showing slag penetration into the particle.
- Figure 4. SEM picture of MgO dipped in slag showing FeO•MgO surrounding MgO.
- Figure 5. EDX spectrum of (a) MgO grains; (b) MgO•FeO layer.
- Figure 6. SEM picture of dolomite dipped into slag showing no slag penetration and CaO being leached away.
- Figure 7. SEM picture showing MgO grains from dolomite dissolving in slag.
- Figure 8. MgO content as a function of time for MgO, MgO plus CaO, and dolomite additions.
- Figure 9. Basicity of the slag as a function of time.
- Figure 10. Amount of material dissolved for additions of magnesite (6.06 g), dolomite (12.13 g) and magnesite plus lime (12.59 g).
- Figure 11. Rate of dissolution of magnesite cylinder for a rotational speed of 200 rpm.

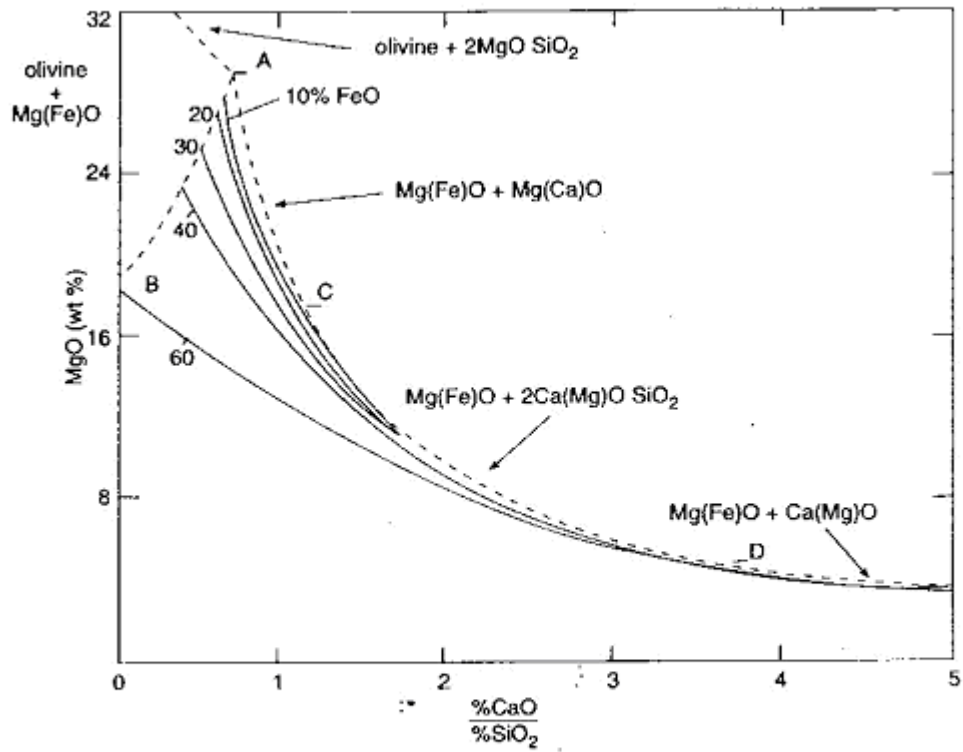


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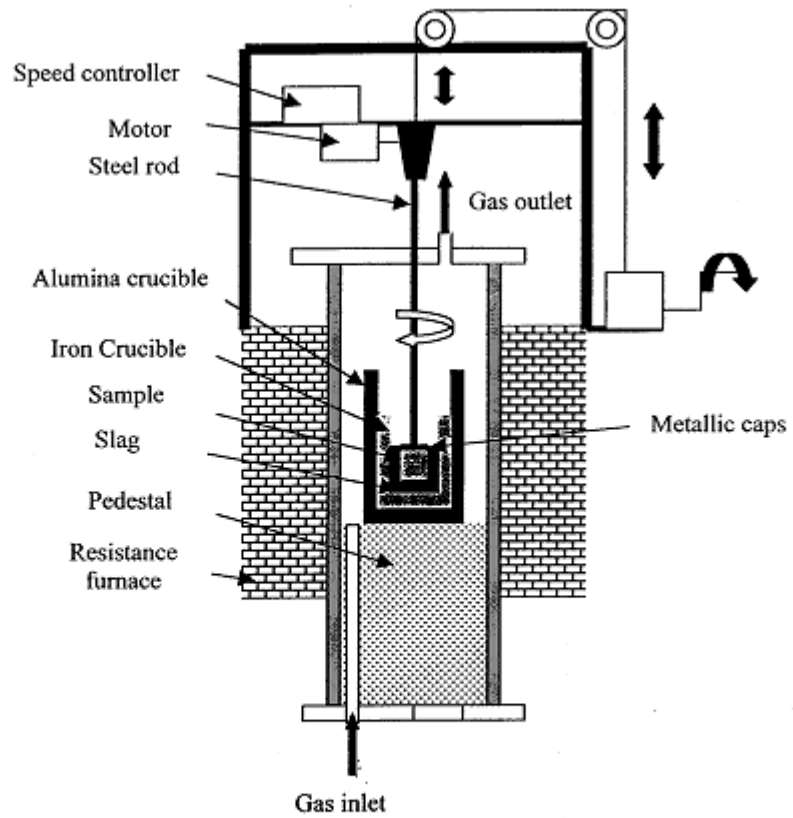


Figure 2. Schematic diagram of rotating cylinder experimental equipment.

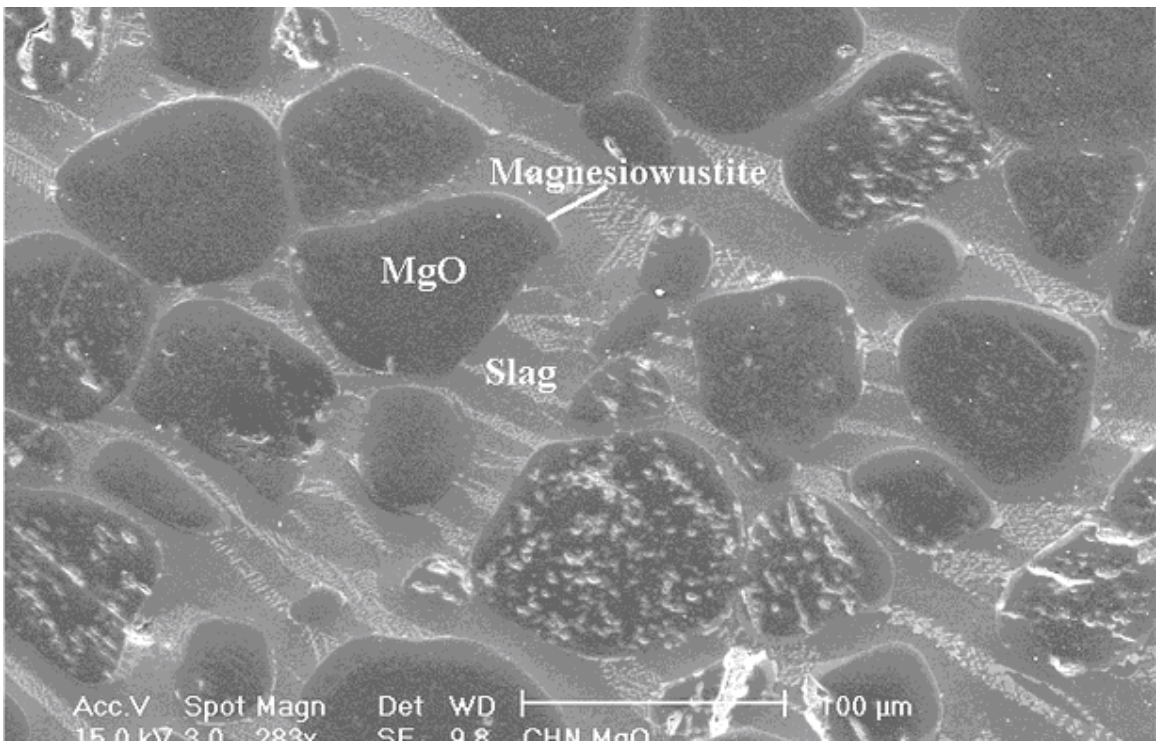


Figure 3. SEM picture of MgO showing slag penetration into the particle.

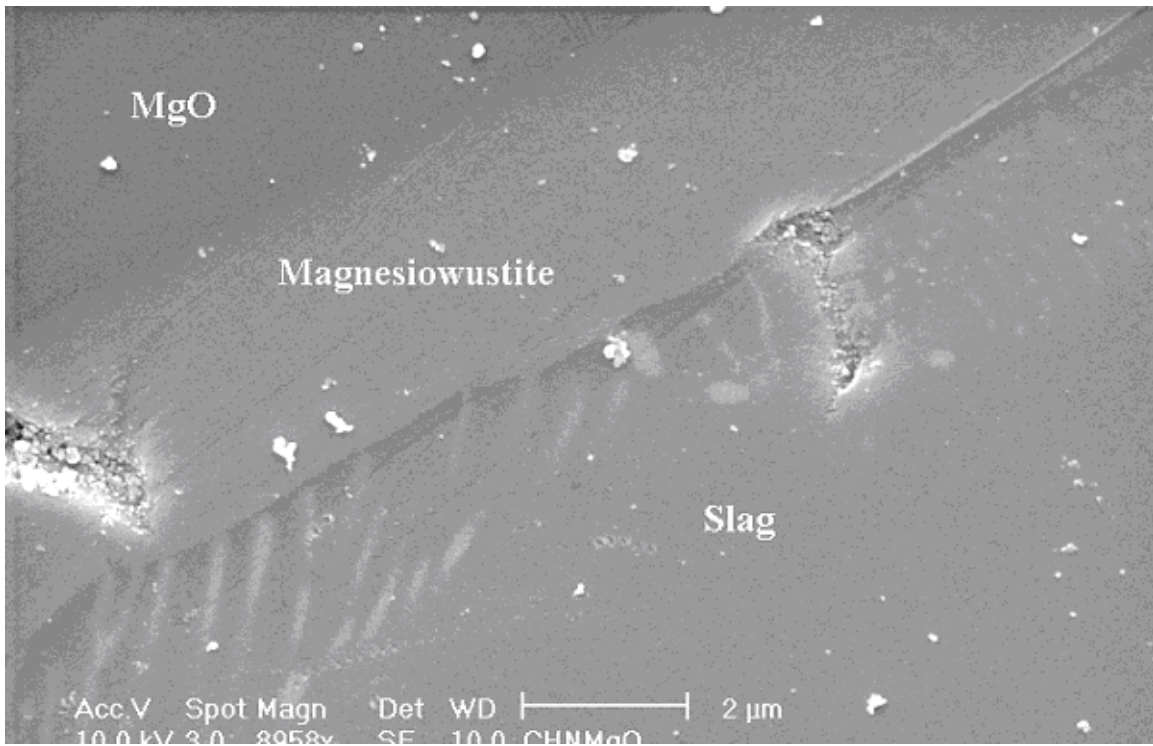


Figure 4. SEM picture of MgO dipped in slag showing FeO•MgO surrounding MgO.

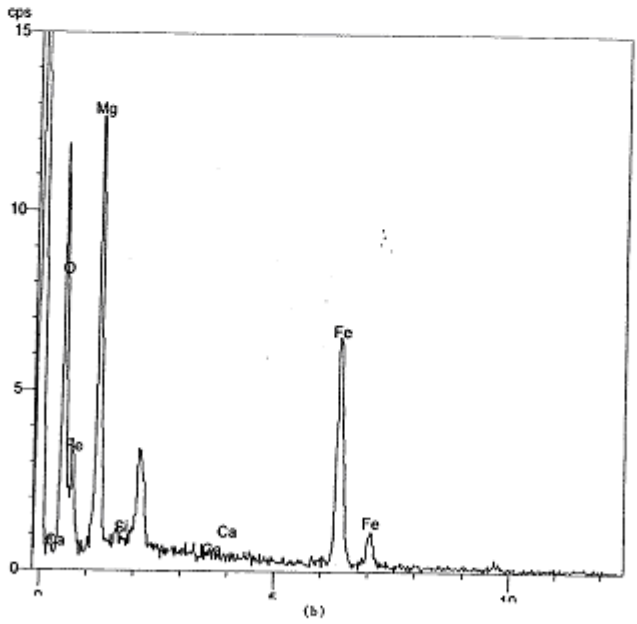
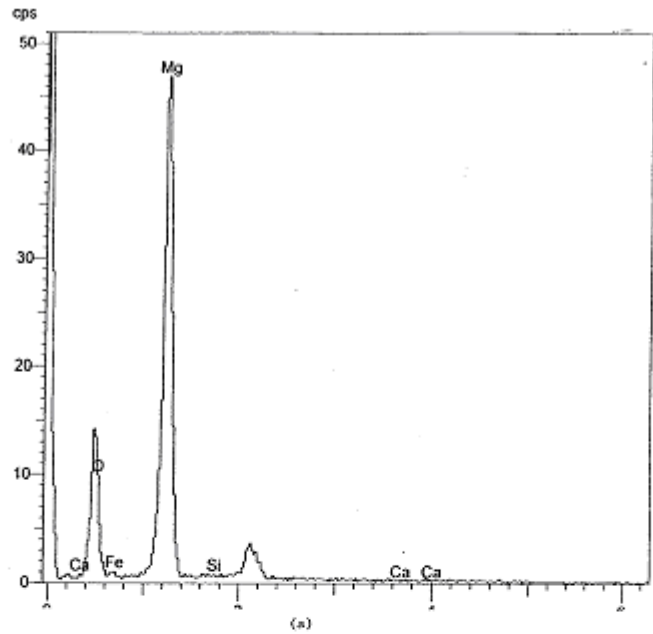


Figure 5. EDX spectrum of (a) MgO grains; (b) MgO•FeO layer.

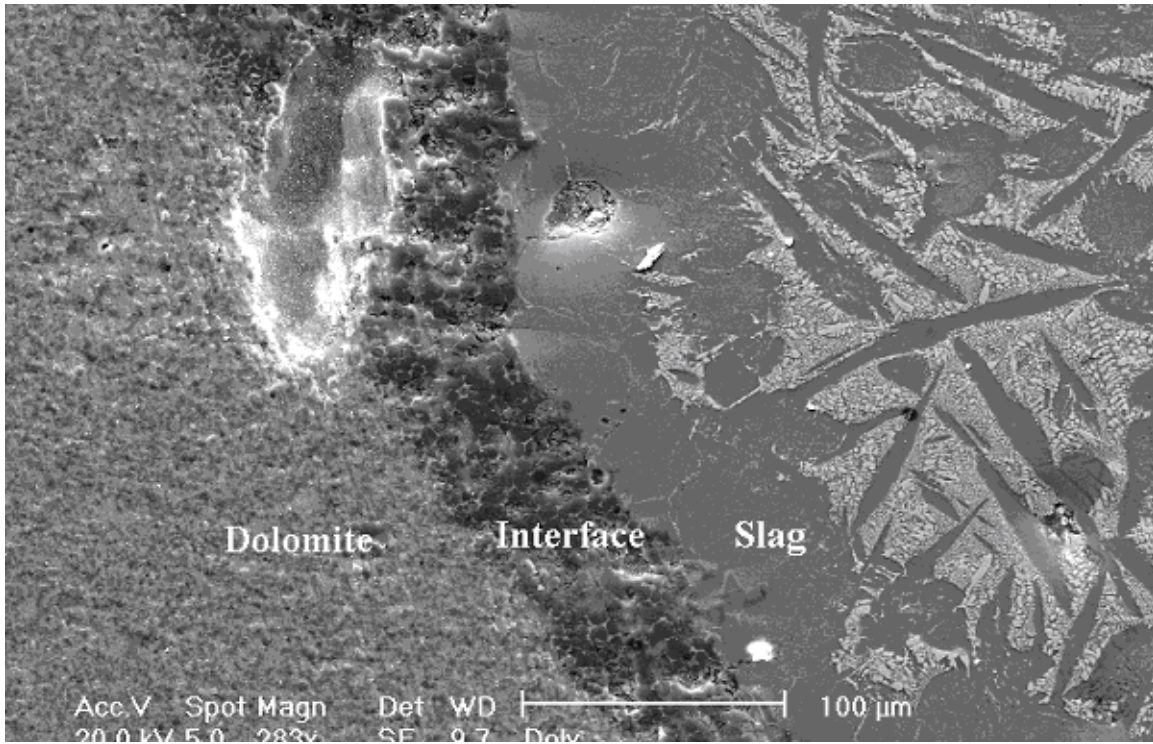


Figure 6. SEM picture of dolomite dipped into slag showing no slag penetration and CaO being leached away.

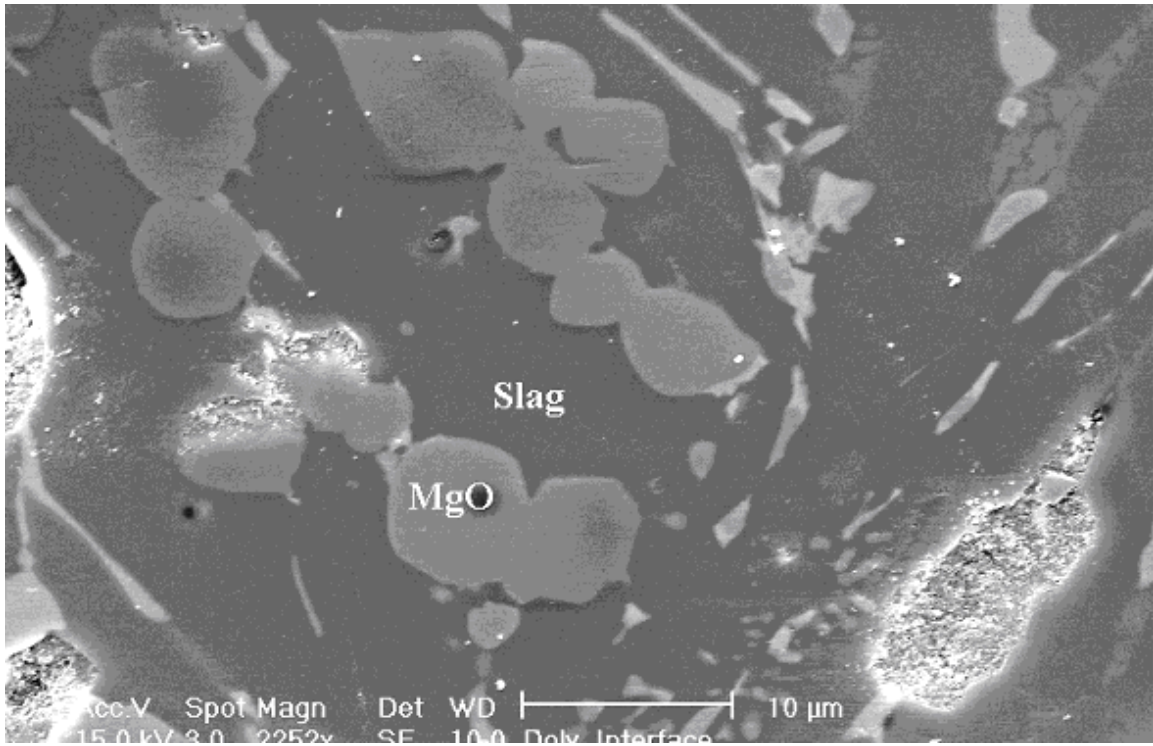


Figure 7. SEM picture showing MgO grains from dolomite dissolving in slag.

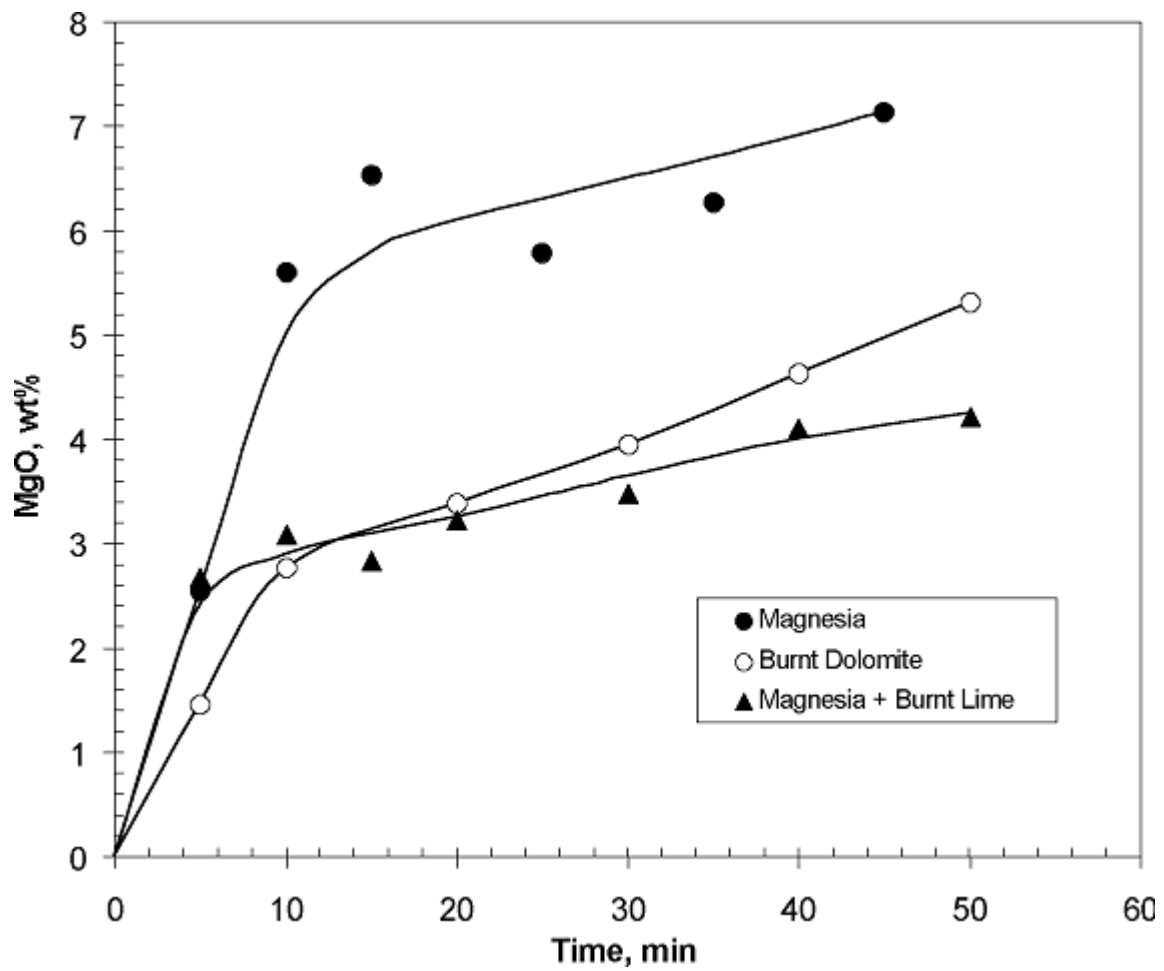


Figure 8. MgO content as a function of time for MgO, MgO plus CaO, and dolomite additions.

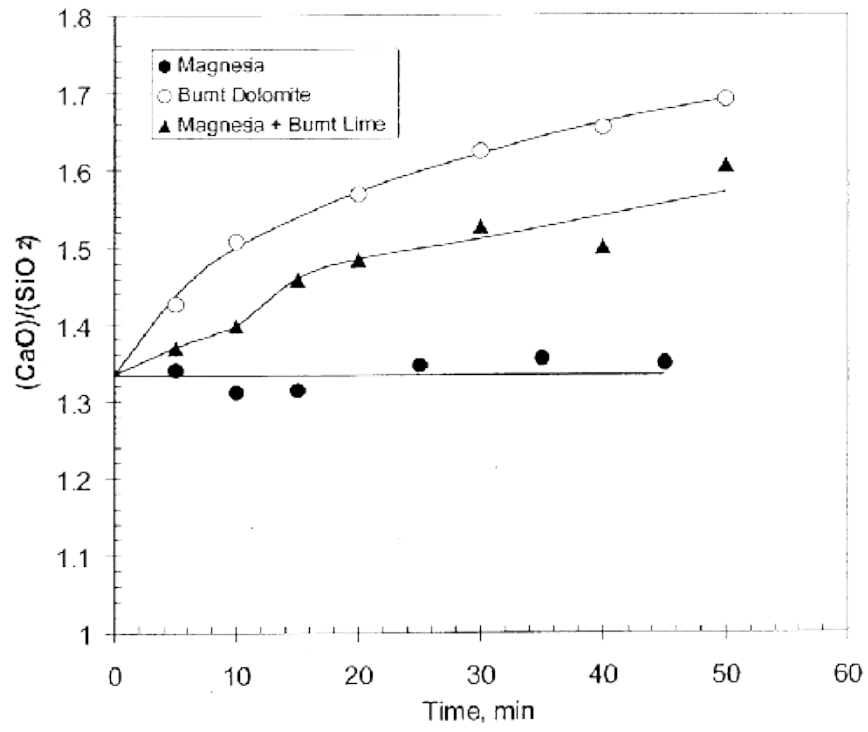


Figure 9. Basicity of the slag as a function of time.

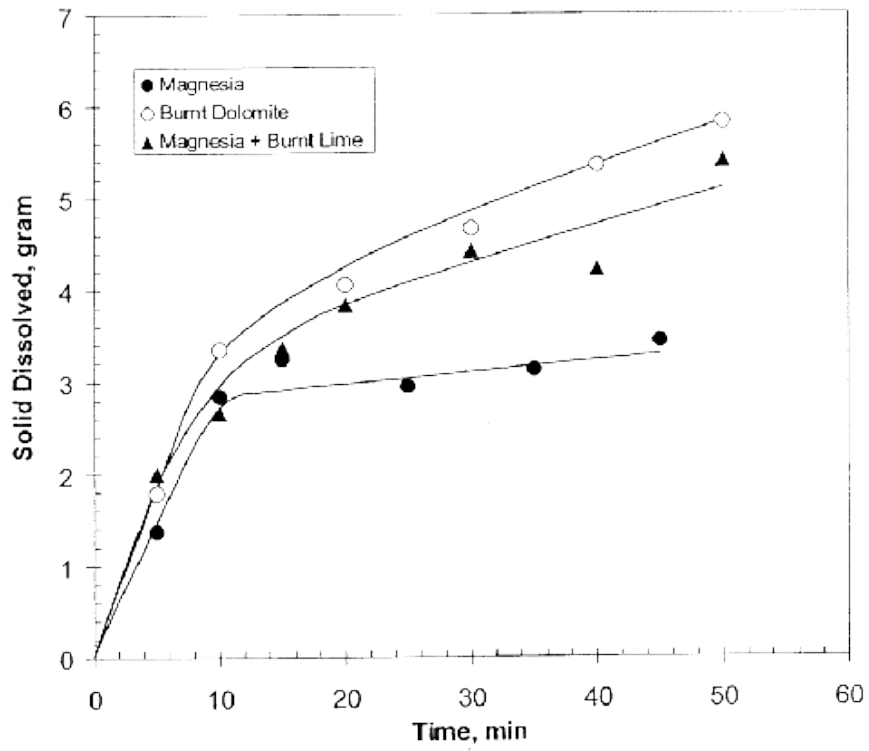


Figure 10. Amount of material dissolved for additions of magnesite (6.06 g), dolomite (12.13 g) and magnesite plus lime (12.59 g).

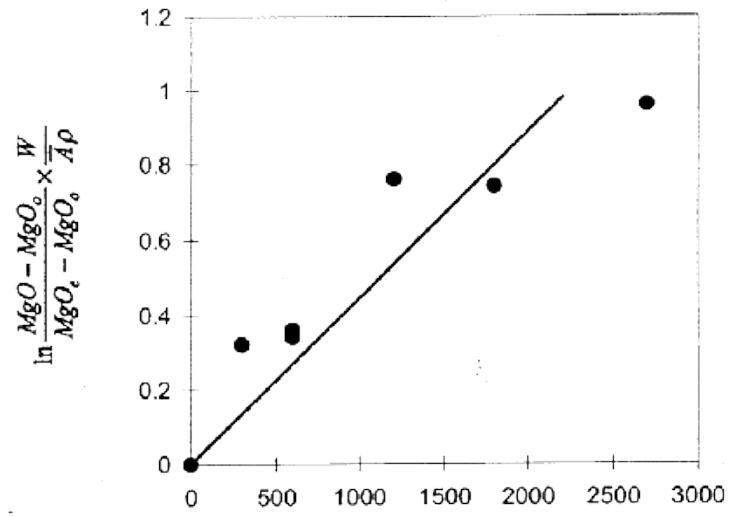


Figure 11. Rate of dissolution of magnesite cylinder for a rotational speed of 200 rpm.