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INSTITUTE OF EARTH RESOURCES

DIVISION OF MINERAL CHEMISTRY

PRODUCTION OF MAGNESIA FROM SAVAGE RIVER MAGNESITE

1979

Carried out on behalf of
Industrial and Mining Investigations Pty Ltd

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J.H. CANTERFORD and P.T. EVERSON

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P.O. Box 124, Port Melbourne
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SUMMARY

The more significant alternative processes for producing magnesium oxide from magnesite/dolomite are briefly reviewed. On the basis of the known chemical and mineralogical characteristics of the Savage River magnesite, it is considered that the calcination/carbon dioxide pressure leach process represents the most technically viable of the alternative processes.

Five samples of Savage River magnesite have been carefully characterized and two of these subjected to a series of laboratory scale calcination tests. The results of these tests have been correlated with the compositions of the samples and are to be used to design technical scale tests to be carried out in the next stage of the overall project.

Leaching tests have commenced and although the tests have not been completed, it is quite apparent that the kinetics of the dissolution reaction are markedly dependent on calcination conditions. Samples calcined at relatively low temperatures are quite reactive and it is possible to produce a concentrated magnesium bicarbonate solution close to saturation under what appear to be technologically and economically viable conditions.

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INTRODUCTION

Magnesium oxide (MgO, magnesia) is an important industrial raw material. The applications of magnesium oxide are dependent upon the grade and chemical reactivity of the material and range from the manufacture of refractories to additives in cosmetic and pharmaceutical formulations. Although magnesium oxide occurs in nature as the mineral periclase, the commercially utilized oxide is derived either from sea water or from minerals with high magnesium contents such as magnesite and dolomite. Whatever the source, the magnesium oxide is obtained by calcination of an intermediate magnesium salt or magnesite itself.

The physical properties of magnesium oxide, particularly specific gravity and surface area, vary greatly with the nature of the material thermally decomposed, the time and temperature of calcination, and the presence of traces of impurities. Temperature and time of calcination have a marked influence on the reactivity of the oxide. Material produced at calcination temperatures below 900°C (caustic-burned magnesia) is relatively easily hydrated with water and dissolves more readily in mineral acids than does oxide prepared at higher temperatures (dead-burned or sinter magnesia).

The market value of magnesium oxide depends on its physical and chemical properties as well as on purity, particularly with respect to its iron content. High grade magnesium oxide has an iron specification of less than 0.15%. The current price of magnesia is of the order of $150-300/tonne.

A rather large, relatively high grade deposit of magnesite has been outlined in the Savage River region of Tasmania, and at the request of Mr. E.R. Hudson of Industrial and Mining Investigations Pty Ltd, the Division has undertaken a detailed study of the production of magnesium oxide from this material. Before discussing the scope of the present study, it is appropriate to outline the alternative processes available.

PRODUCTION OF MAGNESIUM OXIDE

There are three basic approaches to the production of magnesium oxide:

(a) From sea water or brines, using calcium oxide, calcium hydroxide or calcined dolomite to precipitate magnesium hydroxide (1-4):

$$MgCl_2 + CaO + H_2O \longrightarrow Mg(OH)_2 + CaCl_2 \qquad (i)$$

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2 \qquad (ii)$$

$$MgCl_2 + CaO{\cdot}MgO + 2H_2O \longrightarrow 2Mg(OH)_2 + CaCl_2 \qquad (iii)$$

The magnesium hydroxide is thermally decomposed to the oxide. Because of the relatively low magnesium content of sea water (approximately 1.5 gpl), very large volumes of liquid must be processed; the size of the plant negates the very low cost of the sea water or brine. The use of calcined dolomite as the precipitant (reaction iii) obviously increases the yield of magnesium hydroxide per unit volume of sea water or brine, but will increase capital and operating costs. The magnesium hydroxide tends to have a very low settling rate and is relatively difficult to filter. Settling and filtering rates can be increased by the use of flocculants etc., but these tend to have a detrimental effect on product purity.

(b) Physical beneficiation of magnesite/dolomite before or after calcination. The common impurities found in magnesite/dolomite deposits include hematite, quartz, calcite and layer silicates such as talc and serpentine. These impurities normally occur as discrete entities and can be removed by reverse flotation prior to calcination (5) or by heavy media separation after calcination (6). The viability of these techniques depends upon the degree of liberation of the impurities during crushing and grinding.

(c) As noted above, the iron content of the magnesium oxide product has an important bearing on use and market price. In some magnesite/dolomite deposits, iron is present by substitution of iron for magnesium in the magnesite/dolomite crystal lattice. In these

cases it is not possible to remove the iron impurity by physical means and it is necessary to use a complete dissolution technique, the iron-containing impurity remaining in the leach residue or being precipitated from the pregnant leach liquor prior to recovery of the magnesium oxide.

It has been established (7) that the iron in the Savage River magnesite is present in solid solution with the magnesite so that a complete dissolution process represents the only technologically viable process for treating this particular source of magnesium oxide. It is also apparent that, although the deposit contains a small but significant amount of dolomite, the dominant mineral is magnesite. Thus the deposit can be referred to as a magnesite orebody. The relatively low dolomite content is of economic importance since it follows that the amount of solids to be removed from the pregnant leach pulp is small.

DISSOLUTION OF MAGNESITE/DOLOMITE

Numerous processes have been proposed for recovering high grade magnesium oxide from magnesite/dolomite ores involving complete dissolution of the magnesium content, recovery of an insoluble magnesium salt and calcination of the latter. Many magnesites/dolomites tend to be relatively unreactive so that a number of the proposed processes involve a preliminary low temperature calcination stage to ensure reasonably rapid dissolution kinetics. The more important of the dissolution processes include the following:

(a) Sulphuric acid leaching of magnesite (8). Magnesium goes into solution as the water soluble sulphate, and after removal of insoluble impurities (chiefly calcium sulphate), the pregnant liquor is neutralized with magnesia to precipitate iron. Hydrated magnesium sulphate ($MgSO_4 \cdot xH_2O$; x = 1.5-4.0) is recovered by pressure crystallization. The product is thermally decomposed to the oxide, the sulphur dioxide/sulphur trioxide evolved being converted to sulphuric acid in a contact plant for recycling to the leaching stage.

(b) Hydrochloric acid leaching of calcined magnesite (9). This is

essentially the same as the sulphuric acid process; calcination of the magnesite is used to reduce the dissolution of iron as well as increasing magnesium dissolution kinetics. The hydrogen chloride evolved during calcination of the hydrated magnesium chloride is readily recovered as hydrochloric acid of the appropriate strength for recycling to the leaching circuit.

(c) Nitric acid leaching of dolomite (10). Both calcium and iron tend to go into solution as the respective nitrates, necessitating complex purification stages before recovering hydrated magnesium nitrate. A nitric acid plant is necessary to recover the nitrogen oxides during calcination as nitric acid.

(d) Leaching of calcined magnesite/dolomite with carbon dioxide at atmospheric pressure (11-17) or at an elevated pressure (11,13, 18,19). Magnesium oxide reacts with carbonated water to form a solution of magnesium bicarbonate

$$MgO + 2CO_2 + H_2O \longrightarrow Mg(HCO_3)_2 \qquad \text{(iv)}$$

Calcium and iron oxides do not react in a similar fashion to any appreciable extent and these can be filtered off. Magnesium bicarbonate is unstable in the solid state and a hydrated carbonate such as $MgCO_3 \cdot 3H_2O$ (nesquehonite) or a basic carbonate such as $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ (hydromagnesite) can be readily precipitated from the pregnant magnesium bicarbonate solution by lowering the carbon dioxide content of the solution by air sparging and/or heating. The precipitated magnesium carbonate/basic carbonate is readily calcined to the oxide and the carbon dioxide evolved returned directly to the leaching circuit.

Of these four processes, the carbon dioxide leach process has several advantages:

- an acid plant is not required,
- corrosion is reduced, and
- selectivity with respect to dissolution of iron and calcium is highest.

Disadvantages of the carbon dioxide leach process are:

- pre-leach calcination is essential because magnesite itself shows only very limited reactivity with an aqueous solution of carbon dioxide, and
- magnesium bicarbonate is very much less soluble in water than is magnesium sulphate, chloride or nitrate so that the plant size must be substantially greater for the same throughput of magnesium

The solubility of magnesium bicarbonate is markedly dependent on temperature (decreasing with increasing temperature) and carbon dioxide partial pressure (increasing with increasing pressure). Thus by pressure leaching at a relatively low, controlled temperature it should be possible to achieve acceptable dissolution kinetics and pregnant liquor concentrations.

Overall, and particularly in view of the fact that the Savage River magnesite contains an appreciable amount of iron in solid solution with the magnesite, it is considered that carbon dioxide pressure leaching of calcined magnesite represents the most viable of the alternative processes, both technologically and economically.

A simplified, schematic representation of the carbon dioxide pressure leach process is shown in Figure 1. The magnesite ore is dry crushed to a suitable size for calcination either in a rotary kiln or a fluidized bed reactor; coal is probably the best fuel. Calcination conditions must be chosen to ensure maximum yield of reactive magnesium oxide. Following calcination, grinding is carried out to reduce the calcine to a suitable size for leaching. This can probably be selectively carried out, with rejection of hard impurities such as quartz. Wet grinding would be best since it is necessary to cool the calcine in order to carry out leaching at about $20^{\circ}C$. Leaching is carried out on a continuous basis in a series of stirred autoclaves. The carbon dioxide evolved during calcination of the ore and of the precipitated carbonate/basic carbonate would need to be scrubbed and compressed before re-introduction into the leaching circuit. The autoclaves would need to be fitted with

cooling coils to control the exothermic dissolution reaction. After separation of the insoluble residue, the pregnant liquor can be sparged with air to precipitate $MgCO_3 \cdot 3H_2O$ (nesquehonite) or heated above about 50°C to precipitate a basic magnesium bicarbonate. After recovery of the solid product, which is readily calcined to the oxide, the magnesium-containing mother liquor is returned to the leaching circuit. The conditions of the second calcination step are determined by the type of product required - caustic or dead burned magnesia.

SCOPE OF THE PRESENT STUDY

Although many aspects of the carbon dioxide leaching process have been described in the literature, there are virtually no technical or engineering data available which would permit the design of a suitable plant for treating Savage River magnesite. The generation of sufficient data would necessitate detailed laboratory and technical scale studies on representative samples of Savage River magnesite.

Under the terms of the agreement between the Division of Mineral Chemistry and Industrial and Mining Investigations Pty Ltd, the Division is to carry out the following experimental work on suitable samples of Savage River magnesite using the carbon dioxide pressure leach process:

(a) Characterization of magnesite samples. The chemical and mineralogical characterization of the samples provided is essential in order to be able to understand and interpret the results obtained in the chemical processes.

(b) Calcination of magnesite. The effects of time, temperature and particle size on the subsequent leaching steps are to be assessed.

(c) Leaching of calcined magnesite. Parameters which affect the dissolution rate, including time, temperature, carbon dioxide pressure, pulp density, particle size and degree of agitation, are to be investigated in detail and related to the pre-leach calcination conditions.

(d) Recovery of pregnant magnesium bicarbonate solution. This will include determination of settling rates and ease of filtration.

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(e) Precipitation of magnesium carbonate/basic carbonate. The ease of precipitation of a readily filtered product, its identification and characterization, and the possibility of recycling the filtrate after solid-liquid separation are to be determined.

(f) Calcination of the precipitated carbonate/basic carbonate. The influence of time and temperature on the physical and chemical properties of the magnesium oxide product are to be assessed.

Initially the above experimental work is to be carried out using laboratory scale equipment. The data generated from these studies are then to be used to design and/or modify suitable technical scale equipment. Sufficient experimental work will be carried out using this equipment to enable a preliminary economic assessment of the carbon dioxide pressure leach process as applied to Savage River magnesite to be made. This assessment would not involve detailed plant design, but would provide reasonable estimates of the probable unit capital and operating costs.

At present it is anticipated that the laboratory scale studies will take a minimum of six months and that completion of the technical scale study and the associated economic assessment may require an extension of the contract period.

EXPERIMENTAL

MATERIALS

Five composite samples, each approximately 50 kg in weight, were received from the Tasmanian Department of Mines. The composite samples consisted of roughly crushed diamond drill core, the approximate compositions (%) of each sample being

	MgO	CaO
MAG 1	26	23
MAG 2	44	2
MAG 3	41	4
MAG 4	42	4
MAG 5	37	10

These compositions are based on the assays of the fractions making up each composite sample.

The Savage River magnesite orebody apparently consists of magnesite with bands of dolomite interspersed throughout. Samples MAG 2, MAG 3, and MAG 4 represent composites principally composed of magnesite, sample MAG 1 is chiefly dolomite, while sample MAG 5 represents a mixture of magnesite- and dolomite-rich fractions.

Each composite sample was separately spread out on a clean, dry concrete pad and thoroughly mixed. Three separate grab samples of each composite, each of about 100 g, were taken for chemical and mineralogical analysis. These grab samples were dry ground in a laboratory hammer mill to 100% -100 mesh.

In view of the large number of laboratory scale tests considered necessary to generate sufficient data for the design and execution of the technical scale test programme, it was arbitrarily decided to concentrate laboratory scale calcination and leaching tests on samples MAG 1 and MAG 3. These two samples can be considered as representing the two chemical and mineralogical extremes of the Savage River orebody. Samples of intermediate composition, such as MAG 5, should show a reactivity directly related to that of samples MAG 1 and MAG 3.

After mixing and recovery of the grab samples, samples MAG 1 and MAG 3 were split in half, one fraction of each being kept for reference and the technical scale test programme, the other fraction being dry screened, the +¼", -¼"+7 and -7 mesh fractions being collected.* Grab samples (approximately 50 g) of each fraction were collected for chemical and mineralogical characterization. The -¼"+7 mesh fractions represented 60-70% by weight of each composite sample. All of the laboratory scale calcination and leaching tests were carried out using the -¼"+7 mesh fractions. For some of the calcination tests this particle size was used without further size reduction; for a limited number of calcination tests the -¼"+7 mesh samples were dry ground in a laboratory hammer mill to 100% -100 mesh. The calcines derived from the -¼"+7 mesh samples were ground in a similar manner prior to leaching. Sieving of the high temperature calcines was relatively more difficult because of the tendency of the material to absorb moisture

*All mesh sizes are BSS.

CHEMICAL ANALYSIS

The magnesium, calcium and iron contents of the magnesite samples, calcines, leach residues, intermediate and final products, pregnant leach liquors and recycle filtrates were determined by atomic absorption spectrophotometry using the following sample dissolution techniques where appropriate.

- Magnesite samples and intermediate and final products: digestion in dilute hydrochloric acid. The digestion conditions were such that only the carbonate containing minerals were dissolved. Undissolved material in the initial magnesite samples was collected and reported as an acid-insoluble residue.
- Calcines and leach residues: fusion with sodium peroxide-sodium carbonate.

The carbonate contents of the initial magnesite samples, leach residues and intermediate products were determined by combustion in a LECO furnace.

X-RAY DIFFRACTION

All of the magnesite samples and calcines, as well as selected leach residues and intermediate and final products, were analysed by X-ray diffraction using a Philips X-ray diffractometer. Normally the XRD patterns were recorded using fixed operating conditions (sensitivity 4×10^2, time constant = 1, 2°/min) to allow direct comparison of the composition of the samples. Under these conditions, minor fractions of each sample could be identified. The XRD patterns of the calcination products were also recorded under conditions such that the strongest reflection was 90-100% full scale deflection (relative intensity); this was achieved by altering the sensitivity, keeping the time and scan rate constant. These patterns allowed the decomposition of magnesite and dolomite to be carefully followed and related to the weight losses on ignition.

The phases present in each sample analysed were identified by comparison of the recorded patterns with those listed in the ASTM index.

DIFFERENTIAL THERMOGRAVIMETRIC ANALYSIS/THERMOGRAVIMETRIC ANALYSIS

DTA and TGA curves of all of the magnesite samples and of selected leach residues and the intermediate products were recorded using a Rigaku Thermoflex Thermobalance/Differential Thermal Analyzer. Approximately 15 mg of each sample was heated at a rate of 10°C/min in a static air atmosphere. In one experiment the air in the apparatus was flushed out with carbon dioxide and a carbon dioxide atmosphere maintained over the sample during heating by passing a small flow of carbon dioxide through the apparatus during the test.

CALCINATION

250 g samples of the -¼"+7 mesh fractions of MAG 1 and MAG 3 were placed in identical silica dishes and heated at a given temperature for a given time in a preheated electrically heated muffle furnace. Halfway through the heating cycle the positions of the silica dishes within the muffle furnace were reversed to ensure each sample underwent the same heating profile. After removal from the muffle furnace, the samples were cooled slowly to room temperature and the loss in weight on ingition calculated. A number of the calcination tests were repeated with samples of the -¼"+7 mesh fractions that had been dry ground to 100% -100 mesh.

Suitable samples of the intermediate products were calcined in the same furnace at the required temperature.

SURFACE AREA

The surface areas of several of the calcines were determined by nitrogen adsorption (BET method) using a Carlo Erba Series 1800 Sorptomatic instrument.

PRESSURE LEACHING

Equipment

Laboratory scale pressure leaching tests were carried out in an Autoclave Engineers 2 litre stainless steel autoclave (model AFP-2005). The autoclave was initially fitted with an $\frac{1}{8}$" OD

sampling tube and needle valve; in a test run it was found that this readily became blocked by solids settling out of the pulp so it was decided to machine the head of the autoclave to take a ¼" OD sampling tube and replace the needle valve with a quick action ball valve. Even so, it was found necessary to blow out the sampling tube and ball valve with high pressure carbon dioxide after each sampel to prevent build-up of solids in the sampling tube. The Teflon seats of the ball valve were replaced regularly since they became scored and leaked after several kinetic runs.

It is known that the solubility of magnesium ions in a solution saturated with carbon dioxide decreases with increasing temperature, that the kinetics of dissolution of magnesium oxide in such solutions is also influenced by temperature, and that the reactions taking place are exothermic.* To achieve a controlled temperature necessary for kinetic measurements, a refrigerated ethylene glycol-water mixture was pumped through cooling coils of the autoclave. The temperature of the leach pulp was measured with a RIKA indicating temperature controller (model PB-6A1R-M, sensitivity ± 0.1°C). The refrigerated ethylene glycol-water mixture, produced in a modified refrigerated drinking fountain with a 10 litre insulated holding tank, was pumped through a solenoid valve actuated by the indicating temperature controller. If the temperature of the leach pulp was above the set point of the controller then the valve opened and the refrigerated ethylene-glycol mixture passed through the autoclave cooling coils. Once the temperature of the leach pulp was reduced to the required temperature, the solenoid valve was deactivated and the refrigerated ethylene glycol-water mixture returned to the holding tank via a bypass line. In all cases the temperature of the ethylene glycol-water mixture was maintained at least 10°C below the required leach pulp temperature. The heat transfer through the autoclave cooling coils was quite rapid and it was possible to control the leach pulp temperature to ± 0.1°C.

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*As well as the exothermic nature of the dissolution reactions, the temperature of the leach pulp is affected by changes in ambient temperature and by heat generated by mixing. Because the autoclave was well insulated, a change of 5°C in ambient temperature only produced a leach pulp temperature change of 0.2°C. Energy expended during mixing at a stirrer rate of 900 rpm caused a temperature rise of approximately 0.1°C/h.

The magnetically driven stirrer shaft of the autoclave was itself driven by a 0.25 hp electric motor via a flexible drive belt. By altering the pitch circle diameter of the pulley on the electric motor, the autoclave stirrer shaft could be rotated in the range 500-1500 rpm. The stirrer shaft was fitted with a Snyder sub-aerator which drew carbon dioxide from above the level of the leach pulp down through the stirrer shaft, the gas stream being sheared by the blades of the stirrer to form minute bubbles of gas throughout the leach pulp. In this way the leach pulp was continuously saturated with carbon dioxide throughout each leach test.

Procedure

The autoclave and refrigeration system are shown in Figure 2; Figure 3 is a diagrammatic representation of the autoclave. The operation of the autoclave and the collection of leach pulp samples for a typical kinetic run include the following steps:

- One litre of distilled water is added to the clean, dry autoclave which is then raised into position with the pneumatic air leg. The indicating temperature controller is set at the appropriate temperature and the refrigeration unit turned on. The system is then allowed to equilibrate overnight at the required temperature.
- The following morning the autoclave is lowered and a weighed sample of calcined magnesite is carefully added, ensuring that no solid adheres to the walls or baffles of the autoclave.
- The autoclave is raised into position and bolted to the head using a tension wrench. At the operating pressures (0-200 psig) the autoclave is sealed via a Viton "O" ring. During tightening the autoclave is flushed with carbon dioxide by opening valves V3 and V4.
- After tightening and flushing the autoclave, valve V3 is closed, the stirrer motor turned on and the required carbon dioxide pressure adjusted via valve V4.
- High pressure carbon dioxide is blown into the autoclave via the sampling tube and valves V1 and V2. This ensures that there is no leach pulp in the sampling tube and ball valve V2. The working pressure is readjusted via valve V4.

- As the reaction proceeds carbon dioxide is consumed so that the pressure drops; the pressure is continuously monitored and adjusted as necessary by operation of valve V4.

- After the required time interval approximately 5 ml of leach pulp is bled out of the sampling tube by opening valve V2. After noting the volume, the sample is discarded. This sample is taken to ensure that the sample collected for analysis comes from the bulk of the leach pulp and not from within the sampling tube. Approximately 10 ml of leach pulp is then collected in the same manner. This is quickly filtered through a 0.6 micron Millipore filter (without washing) into a clean dry flask kept at $0^{o}C$ in an ice bath. 5 ml of the filtered pregnant leach liquor is recovered by pipette and made up to volume for analysis.* The sampling tube is blown free of leach pulp with high pressure carbon dioxide by opening valves V1 and V2. Valves V1 and V2 were closed when the pressure reached approximately 25 psig above the operating pressure. The pressure is readjusted to the operating pressure by venting excess carbon dioxide through valve V3.

- After the required time intervals, further bleed and analytical leach pulp samples are collected as above.

- At the end of the kinetic run the stirrer motor is turned off and valve V3 opened. The autoclave is unbolted and lowered using the pneumatic air leg, and the pregnant leach pulp recovered and filtered as quickly as possible. The clarified pregnant leach liquor is stored for recovery of an intermediate product while the leach residue is either dried at $110^{o}C$ for chemical and mineralogical analysis, or discarded.

- The cooling coils, thermowell, sampling tube, stirrer, baffles

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*In the first few tests a given volume of leach pulp was collected in a graduated cylinder containing a known volume (about 10 ml) of ice cold water. After filtration, the pregnant liquor was made up to volume. Because of the turbidity of the leach pulp, the volume was difficult to read and it was felt that this could lead to a significant experimental error. Another source of experimental error was eliminated by the use of a Millipore filter system with a 0.6 micron polyvinyl membrane rather than a conventional Buchner funnel and paper filter. It was found that the finest paper filter available would not hold back the very fine solids in suspension whereas these were retained on the Millipore filter and thus did not contaminate the filtrate for analysis.

and autoclave are carefully cleaned and dried for the next dissolution test.

THERMODYNAMIC CALCULATIONS

The heats of various calcination and dissolution reactions were calculated using the REACT program of the CSIRO THERMODATA system (20). Solubility data as a function of temperature and carbon dioxide pressure were taken from various literature sources.

RESULTS AND DISCUSSION

CHARACTERIZATION OF MAGNESITE SAMPLES

The chemical analyses of the three grab samples of the five composite magnesite samples are given in Table 1. As would be expected, there are small differences in the compositions of the three grab samples of each composite arising from non-homogeneity. The data are consistent with the estimated contents provided by the Tasmanian Department of Mines and also indicate that the composite samples contain > 90% carbonate minerals. The chemical analyses (%) of sized fractions of MAG 1 and MAG 3 composite samples are given in Table 2.

The X-ray diffraction patterns of composite samples MAG 1a --- MAG 5a are shown in Figure 4. Table 3 shows the mineral assemblages of the composites deduced on the basis of the relative intensities of the diagnostic reflections.* The X-ray diffraction pattern of the sized fractions of MAG 1 and MAG 3 show minor changes in the relative intensities of the major reflections - Figure 5 shows the patterns of the MAG 1 sized fractions. The X-ray diffraction data of the sized and unsized grab samples are consistent with the chemical analyses shown in Tables 1 and 2. This confirms that the patterns are capable of providing a rapid indication of sample composition.

X-ray diffraction patterns of the acid insoluble residues

*The reflections of the talc mineral, whose composition was not deduced, are subject to orientation effects and are often enhanced, which may lead to an apparently high talc content.

after hydrochloric acid digestion showed them to be primarily quartz with a small amount of talc.

Composite sample MAG 1 was light grey in colour while the remaining samples were "white" with a small and variable amount of iron staining.

CALCINATION OF MAGNESITE SAMPLES

As noted previously, it is necessary to calcine the magnesite to magnesium oxide prior to carbon dioxide leaching to ensure reasonably rapid kinetics. Calcination conditions need to be defined carefully to ensure maximum decomposition of magnesium carbonate to an oxide with maximum reactivity with respect to dissolution. Magnesite, calcite and siderite decompose according to the following reactions:

$$MgCO_3 \longrightarrow MgO + CO_2 \qquad (v)$$

$$CaCO_3 \longrightarrow CaO + CO_2 \qquad (vi)$$

$$FeCO_3 + 0.25O_2 \longrightarrow 0.5Fe_2O_3 + CO_2 \qquad (vii)$$

Dolomite undergoes the following overall decomposition reaction:

$$MgCa(CO_3)_2 \longrightarrow MgO + CaO + 2CO_2 \qquad (viii)$$

There is considerable evidence (21) that in fact dolomite decomposes in two stages:

$$MgCa(CO_3)_2 \longrightarrow MgO + CaCO_3 + CO_2 \qquad (ix)$$

$$MgO + CaCO_3 \longrightarrow MgO + CaO + CO_2 \qquad (x)$$

With the exception of reaction (vii), these reactions are endothermic, that is, they require heat. The heats of reactions (v) --- (viii) per mole of $MgCO_3$, $CaCO_3$, $FeCO_3$ and $MgCa(CO_3)_2$ as a function of temperature are given in Table 4. The temperature at which the above decomposition reactions take place depends on particle size, degree of crystallinity, atmosphere and heating rate but are of the order of 700, 950, 600, 700 and 950°C respectively for reactions (v), (vi), (vii), (ix) and (x).

Differential Thermal and Thermogravimetric Analysis

The differential thermal analysis and thermogravimetric analysis curves show the heat and weight losses of the decomposition reactions of the composite samples MAG 1a --- MAG 5a in a static air atmosphere, as well as those of MAG 3a in a flowing carbon dioxide atmosphere. Figure 6 shows the curves of MAG 1a in static air and of MAG 3a in static air and flowing carbon dioxide. The curves of MAG 2a, MAG 4a and MAG 5a in static air are essentially the same as those of MAG 3a in static air. The differences between the curves of MAG 1a and MAG 3a in static air are immediately apparent and can be related to the mineralogical composition of the samples. The differences in the curves caused by the different atmospheres above sample MAG 3a during heating are also apparent.

All of the differential thermal analysis and thermogravimetric analysis curves show three endothermic peaks and associated weight losses. The amount of iron present in the composite samples is quite low (Table 1) indicating a low iron carbonate content. Thus the curves can be considered as being caused by:

(a) Decomposition of magnesite

$$\text{magnesite} + \text{dolomite} + \text{calcite} \longrightarrow \text{dolomite} + \text{calcite} + MgO + CO_2$$

(b) Decomposition of the $McCO_3$ portion of the dolomite

$$\text{dolomite} + \text{calcite} + MgO \longrightarrow \text{calcite} + MgO + CO_2$$

(c) Decomposition of the calcite portion of the dolomite and any free calcite

$$\text{calcite} + MgO \longrightarrow CaO + MgO + CO_2$$

Assuming the dolomite has a magnesium to calcium ratio of unity, which is normally the case with natural dolomites, it is possible to calculate the mineralogical composition of the samples using the weight loss data. In these calculations it is necessary to consider the possible errors introduced by the decomposition reactions of the minor phases.

- Quartz undergoes a structural change ($\alpha \rightarrow \beta$ transition) at about $573^{o}C$ - this is indicated by a small endotherm. There is, of

course, no associated weight loss with this transition. In all of the composite magnesite samples this endotherm would be masked by the more intense magnesite decomposition endotherm.

- Talc dehydroxylates at high temperatures and this would tend to give high weight losses, particularly in the third decomposition stage. However, the low talc contents of the samples, as indicated by the X-ray diffraction patterns of the original composites and acid soluble residues, suggests that the error due to the presence of talc would be quite small and can be consequently ignored in the mineral composition calculations.

- The available literature (21) indicates that whether the iron is present as a simple carbonate [siderite, $FeCO_3$], a complex carbonate [pistomesite, $FeMg(CO_3)_2$] or in solid solution with magnesite, the iron carbonate will decompose at a temperature slightly lower than that of magnesite. The calculations have thus been corrected to allow for the presence of iron carbonate by reducing the magnesite content by an amount equivalent to the chemically determined iron content.

The differential thermal analysis peak positions, thermogravimetric analysis curve weight losses, the corresponding uncorrected and converted mineral compositions, the elemental composition corresponding to the corrected mineral composition and the chemical analysis data are given in Table 5. There is good agreement between the elemental compositions derived from the differential thermal analysis and thermogravimetric analysis curves and the chemical analysis data indicating that the assumptions made in deriving the first set of data are not greatly in error.

The differential thermal analysis and thermogravimetric analysis data clearly indicate that it is necessary to heat the Savage River magnesite to at least 700°C to ensure that the magnesite is decomposed to magnesium oxide. If the sample contains an appreciable amount of dolomite then it will, for economic reasons, be necessary to recover the magnesium content of the dolomite. This means that the magnesite content of the dolomite must be decomposed. This requires a calcination temperature of 750-800°C. Since

calcination is an energy intensive unit process, it is essential that optimum conditions be accurately determined with representative samples. It is known that a lower heating rate tends to reduce the maximum temperature required for complete decomposition so there has to be a compromise between calcination time and calcination temperature.

The carbon dioxide atmosphere test on sample MAG 3a confirms reports (11,12) that the atmosphere above the sample has an important effect on decomposition temperatures. In the present case, the artificially applied carbon dioxide atmosphere affects the kinetics and temperatures of the decomposition reactions. For both the free magnesite and the magnesite component of the dolomite, the decomposition temperature is increased by 60-70°C while for the calcite component of the dolomite the decomposition temperature is increased by 140-150°C. At present no suitable explanation has been found for the broadening of the second differential thermal analysis peak in the carbon dioxide atmosphere test. The increased decomposition temperatures indicate that in the technical scale tests, as well as in the commercial plant, it will be essential to continuously sweep the carbon dioxide out of the calcination kiln.

Muffle Calcination Tests

The effects of time, temperature and particle size on the weight loss on calcination of samples MAG 1 and MAG 3 (muffle tests) are shown in Tables 6 and 7. Also shown in Tables 6 and 7 are the relative intensity ratios of the principal X-ray diffraction reflections of magnesite, dolomite, magnesium oxide and calcium oxide. Figures 7 and 8 show the weight loss as a function of time and temperature respectively. Figures 9-12 show the X-ray diffraction patterns of the calcines derived from the -¼"+7 mesh fractions ground to 100% -100 mesh. From the data presented in Tables 6 and 7 and Figures 7-12, the following conclusions can be drawn:

- For a given time, weight loss increases as temperature increases and for a given temperature, weight loss increases as time increases.

- The overall weight loss of MAG 3 is greater than that of MAG 1; this is consistent with the higher carbonate content of the former.

- MAG 3 reaches its theoretical weight loss more rapidly as the temperature increases than does MAG 1.

- For a given temperature, there is virtually no change in weight loss on ignition after 1.5-2 hours even though the calcination reaction may not have proceeded to completion.

- For a given set of calcination conditions, the loss in weight of the fine material is less than that of the coarse sample. This is because of the lower heat transfer properties of the finer material.

- The temperature required to reach the theoretical weight loss is lower for MAG 3 than it is for MAG 1. This is consistent with the fact that MAG 1 has a significant dolomite content, which requires a higher decomposition temperature.

The data in Tables 6 and 7 and Figures 7-12 are consistent with the known greater thermal stability of dolomite compared with magnesite and the thermogravimetric data (Table 5 and Figure 6). For example, the weight loss of MAG 1 at 970°C from the muffle and thermogravimetric tests are 44.8% and 43.6% respectively.

During calcination there are several noticeable changes in the physical properties of the initial magnesite samples:

- Above about 500°C the colour of the major portion of the samples changes from grey/white to a light brown. Some of the particles do not change colour.

- The particle size of the calcined material is considerably reduced.

- Many of the larger particles show the development of cracks.

- The hardness of the calcined samples is considerably reduced.

These changes, which are shown in Figures 13 and 14, are

consistent with the oxidation of ferrous iron to ferric iron [reaction (vii)] and a loss in weight of up to about 50%, the latter causing a reduction in sample volume. The particles which remained hard and white were shown to be quartz. The lower heat transfer properties of material ground to 100% -100 mesh were quite apparent on sectioning the sample bed; the colour graded from light brown at the upper surface to white at the bottom of the sample.

It is well known (22) that the physical and chemical properties of materials formed by thermal decomposition reactions are markedly dependent on the heating profile used. Magnesium oxide formed by decomposition of magnesium hydroxide, magnesium carbonates/basic carbonates, etc. has been shown to have a surface area dependent on the temperature of preparation; the time of heating has a less marked effect (23,24). Similar effects were observed in the present study for the product formed on decomposition of MAG 3 (-¼"+7 mesh ground to 100% -100 mesh); Figure 15 shows surface area as a function of temperature. The surface area rapidly decreases as the calcination temperature is increased from 590° to 850°C; above this temperature there is only a slight reduction in surface area. Since chemical reactivity is dependent upon surface area, it is to be expected that calcination conditions will have an appreciable effect on the kinetics of the carbon dioxide pressure leaching reactions.

CARBON DIOXIDE PRESSURE LEACHING OF CALCINES

Theoretical Considerations

Considering only the magnesium oxide content of the calcine, the following reactions take place during leaching:

$$MgO + 2CO_2(g) + H_2O \longrightarrow Mg^{++}(aq) + 2HCO_3^-(aq) \qquad \text{(xi)}$$

$$MgO + H_2O \longrightarrow Mg(OH)_2 \qquad \text{(xii)}$$

Both of these reactions are exothermic; at 25°C the heats of reaction are respectively 41.4 and 8.89 kcal/mole. Thus the dissolution of 40 g magnesium oxide in 1 litre of water saturated with carbon

dioxide could produce a temperature rise of approximately 40°C*.

Magnesium bicarbonate is stable only in solution and the anount formed in solution is determined by the solubility of the solid phase formed.†

$$MgCO_3 \cdot 3H_2O + CO_2(g) \longrightarrow Mg^{++}(aq) + 2HCO_3^-(aq) + 3H_2O \qquad \text{(xiii)}$$

Assuming unit activity coefficients and ignoring the formation of $CO_3^=$ anions and any complexing by $Mg(HCO_3)^-$, it can be shown that the concentration of magnesium ions in solution is proportional to the cube root of the carbon dioxide partial pressure, i.e.

$$[Mg^{++}] \propto P[CO_2]^{1/3}$$

Yanat'eva and Rassonskaya (25) have studied the $MgCO_3$-H_2O and $CaCO_3$-$MgCO_3$-H_2O systems at a carbon dioxide partial pressure of approximately 100 Kpa (1 atmosphere). Using their data and the above relationship, the solubility of magnesium (expressed as gpl) as a function of carbon dioxide partial pressure and temperature is shown in Figure 16. Also included in Figure 16 are the experimentally determined solubility data of Doerner and coworkers (11). It is quite apparent that there is good agreement between the calculated and experimental data. From Figure 16 it can be seen that solubility increases as the carbon dioxide partial pressure and the temperature increase and decrease respectively. This indicates that from a solubility point of view, leaching should be carried out at as low a temperature and high a pressure as practical. However, the situation is complicated by the fact that it is possible to form a supersaturated magnesium bicarbonate solution (11). This arises because the reaction producing soluble magnesium bicarbonate

$$MgO + 2CO_2(g) + H_2O \longrightarrow Mg^{++}(aq) + 2HCO_3^-(aq) \qquad \text{(xiii)}$$

involves two separate reactions

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*The heat of reaction does not give any indication of the rate at which this heat is generated; it also assumes that there are no heat losses.

†Above about 15°C, $MgCO_3 \cdot 3H_2O$ is the stable phase - below this temperature, $MgCO_3 \cdot 5H_2O$ is formed.

$$MgO + xH_2O + CO_2 \longrightarrow MgCO_3 \cdot xH_2O \qquad \text{(xiv)}$$

$$MgCO_3\ \ H_2O + CO_2 \longrightarrow Mg^{++}(aq) + 2HCO_3^-(aq) \qquad \text{(xv)}$$

If reaction (xv) removes the product of reaction (xiv) as fast as it is formed, then for all practical purposes no crystals of hydrated carbonate are present. Thus supersaturation could lead to severe operating problems since a change in operating conditions may result in precipitation of hydrated magnesium carbonate, $MgCO_3 \cdot xH_2O$, from the pregnant leach liquor. Moreover, it is known (11) that an excess of magnesium oxide will precipitate $MgCO_3 \cdot xH_2O$ from bicarbonate solution; this precipitate will accelerate a reversal of reaction (xv) if the solution is supersaturated. It is possible, however, that supersaturation could also be beneficial under certain operating conditions.

The solubility of calcium oxide in leach liquors saturated with carbon dioxide has been shown by Yanat'eva and Rassonskaya (25) to be considerably lower than that of magnesium oxide. In addition, calcium solubility is at a minimum for a given temperature and carbon dioxide partial pressure when the solution is saturated with respect to magnesium carbonate. For a saturated magnesium carbonate solution the solubility of magnesium is approximately 100 times greater than that of calcium.

For the carbon dioxide pressure leach process, the rate of formation of a pregnant leach liquor will be controlled by:

calcination conditions
time
temperature
carbon dioxide pressure
pulp density
agitation
leach liquor composition

The kinetics of the dissolution reaction [reaction (xi)] need to be accurately determined in order to

(a) choose a set of standard leaching conditions for determining the effects of the above parameters and to allow comparison of the

reactivity of different magnesite samples, and

(b) provide data for design and cost estimation purposes.

Results

For the kinetic studies, bulk samples of MAG 3(-¼"+7 mesh ground to 100% -100 mesh) were calcined in the muffle furnace under the following conditions:

950°	16 h
700°	3 h

Before the kinetic data are discussed, the following points are to be noted:

- With the 700°C calcines the pressure dropped quite rapidly for the first two hours or so necessitating almost continuous readjustment of the pressure to the required value. After this period the rate of pressure drop was much lower and towards the end of a kinetic run (after 5-8 hours) there was virtually no pressure drop.

- With the 950°C calcine the pressure dropped slowly during the whole leaching period.

- The solids in the leach pulp samples settled quite rapidly although the leach pulp samples became progressively more difficult to filter. There was also a progressive darkening of the colour of the filtered solid residue.

- At the end of each leach test the pregnant leach pulp was recovered from the autoclave and the solids filtered off. Some of the residue was extremely fine and it was normally necessary to refilter the first filtrate.

- All of the clarified leach liquors were stored (either separately or bulked) for later recovery of intermediate and final products. Appropriate leach residues were recovered for chemical and mineralogical characterization.

The data for the 950°C/16 h calcine are presented in Table 8 and Figures 17 and 18; the following conclusions can be drawn:

- At an uncontrolled temperature of approximately 20°C, the rate of the dissolution reaction increases as the carbon dioxide partial pressure is increased from 50 psig to 100 psig. A further increase to 125 psig has no effect on kinetics.

- At a carbon dioxide partial pressure of 100 psig an increase in temperature slowly increases the rate of reaction. At 13.5°C the reaction is still proceeding slowly, even after 24 hours.

- For these particular calcination conditions, maximum dissolution achieved is about 20% of the total available magnesium.

- A maximum magnesium concentration of 2 gpl is not practical, nor is the extended time required to achieve this concentration.

Leaching data for the 700°C calcines are not complete but it should be pointed out that pregnant liquors containing in excess of 8 gpl magnesium (that is, approaching saturation) have been obtained after about 2 hours when operating at about 20°C and carbon dioxide at 100 psig. Such a concentration represents about 85-90% dissolution of the total available magnesium. The leaching data for the 700°C calcines will be discussed in detail in the next quarterly report. The large difference in the behaviour of the 950°C and 700°C calcines is consistent with the fact that the 950°C calcine has a much smaller surface area than that produced at 700°C. The results clearly indicate that the dissolution of the magnesium oxide in the calcine is markedly dependent on the calcination conditions.

SUMMARY OF RESULTS/GENERAL CONCLUSIONS

- X-ray diffraction readily indicates the dolomite to magnesite ratio of each ore sample.

- The ore should be crushed to a small enough size to permit even yet 'complete' calcination. Heat transfer and solid flow properties during calcination would also influence the best ore size.

- On calcination there is a reduction in weight and bulk volume of about 50% and 10% respectively. During calcination there is also a marked reduction both in particle size and hardness. These

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factors indicate that grinding to a suitable particle size for leaching would be carried out most economically after calcination.

- Any quartz present in the ore can be removed by selective grinding and screening of the calcine. This reduces the overall load on the grinding circuit as well as reducing the amount of solids that have to be removed from the pregnant leach pulp.

- Dolomite is thermally more stable than magnesite. Moreover, the temperature required to decompose the magnesium carbonate content of the dolomite is greater than that of the magnesium carbonate present as magnesite.

- Surface area and hence chemical reactivity are dependent upon the time and temperature of calcination. To obtain a reactive product it appears that a lower temperature but longer time are more appropriate than a higher temperature for a shorter time.

- To ensure that the calcine has a suitably high chemical reactivity for leaching, it would be advantageous to keep the dolomite content of the ore as low as possible. This would increase the proportion of the leach feed which would be dissolved and thus decrease the amount of unreacted residue that has to be removed from the pregnant leach pulp.

- It is advantageous to remove the carbon dioxide surrounding the ore during calcination since this lowers the temperature necessary for 'complete' decomposition. However, as the carbon dioxide is to be recovered and used in the leaching stage, it should not be diluted too much.

- The kinetics of the dissolution of the magnesium oxide component of the calcine are markedly dependent on the calcination conditions.

- For high temperature (950°C) calcine, leaching at room temperature with a moderate carbon dioxide pressure is more appropriate than at a lower temperature even though the solubility of magnesium carbonate is higher at the lower temperature.

- For low temperature (700°C) calcine, it is possible to dissolve about 90% of the available magnesium in a relatively short time

yielding a solution which approaches saturation with respect to magnesium carbonate.

PROPOSED FUTURE WORK PROGRAMME

In the next three month period it is anticipated that the following will be carried out:

- Completion of laboratory scale leaching tests including the effects of particle size, pulp density, agitation and leach liquor composition.
- Recovery and characterization of intermediate and final products (hydrated magnesium carbonate and magnesium oxide respectively) from clarified pregnant leach liquors.
- Standard leach tests on calcines formed under different conditions.
- Testing of technical scale rotary kiln with particular emphasis on retention time, temperature profile and atmosphere.
- Determination and, if possible, carrying out of the necessary modifications to the technical scale autoclave rig to suit the present process.*
- Compilation of data for capital and operating cost estimates.

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*These modifications are likely to be considerable since the rig has previously been used for pressure leaching of lead-zinc sulphide concentrates at elevated temperatures. New temperature controllers, solenoid valves, pumps, etc., as well as a refrigeration system, will be required for the present study.

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TABLE 1

Chemical Analyses (%) of Magnesite Composite Samples

	Mg	Ca	Fe	CO_3	Acid insoluble	Total
1a	12.7	17.9	0.870	62.0	6.75	100.2
1b	12.4	17.3	0.899	63.0	8.23	101.8
1c	12.6	16.5	0.859	60.0	8.67	98.6
2a	25.0	1.65	1.81	72.0	0.995	101.5
2b	25.2	2.06	1.79	70.5	0.828	100.4
2c	25.5	1.63	1.73	69.5	1.47	99.8
3a	23.6	3.30	1.78	69.0	3.38	101.1
3b	23.3	3.49	1.74	67.5	5.45	101.5
3c	24.3	3.22	1.77	67.5	3.97	100.8
4a	24.9	2.44	1.25	67.0	1.41	97.0
4b	25.2	2.61	1.18	69.5	1.58	100.1
4c	25.6	2.45	1.20	70.5	2.01	101.8
5a	20.3	7.75	1.36	66.0	5.16	100.6
5b	21.6	6.02	1.33	66.0	5.74	100.7
5c	19.9	7.32	1.34	62.5	9.05	100.1

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TABLE 2

Chemical Analyses (%) as a Function of Particle Size

		Mg	Ca	Fe	CO_3	Acid insoluble	Total
MAG 1	+¼"	12.2	17.7	0.871	59.0	9.85	99.6
	-¼" +7 mesh	12.8	17.7	0.915	61.5	5.82	98.5
	-7 mesh	12.5	16.7	0.952	61.5	7.81	99.5
MAG 3	+¼"	22.9	3.78	1.80	68.5	4.67	101.7
	-¼" +7 mesh	23.6	3.34	1.84	67.5	3.27	99.6
	-7 mesh	23.6	3.41	1.80	68.5	3.32	100.6

TABLE 3

Mineral Assemblages of Composite Magnesite Samples

Sample	> 66%	66-33%	33-10%	< 10%
1a	dolomite			calcite, magnesite, quartz, talc
2a	magnesite			dolomite, quartz, talc
3a	magnesite		dolomite	quartz, talc
4a	magnesite			dolomite, quartz, talc
5a		magnesite, dolomite		quartz, talc

TABLE 4

Heats of Thermal Decomposition Reactions (kcal/mole)

Initial material	Temperature (°C)				
	600	700	800	900	1000
Magnesite	26.17	25.48	24.78	24.05	23.31
Calcite	41.05	40.62	40.16	39.67	39.16
Siderite	- 17.14	- 17.27	- 18.36	- 19.78	- 21.44
Dolomite	71.35	70.82	70.15	69.36	68.44

TABLE 5

Differential Thermal Analysis and Thermogravimetric Analysis Data

Sample		1a	2a	3a	3a	4a	5a
Atmosphere		air	air	air	CO_2	air	air
DTA peak °C	1	572	641	634	701	650	631
	2	790	742	738	758-822	735	735
	3	838	851	790	939	809	818
TGA weight loss %	1	4.2	46.1	40.5	40.5	44.2	30.5
	2	23.0	48.1	44.3	44.5	47.0	38.2
	3	43.6	50.0	48.3	49.0	49.8	46.3
Mineral composition from TGA %	magnesite	8.1	88.3	77.6	77.6	84.7	58.4
	dolomite	78.8	8.1	15.9	16.8	11.8	32.2
	calcite	4.1	- [a]	0.5	1.1	-	0.9
	balance	9.0	3.6	6.0	4.5	3.5	8.5
Corrected mineral composition %	siderite [b]	1.8	3.7	3.6	3.6	2.6	2.8
	magnesite	67	85.6	75.0	75.0	82.8	56.3
	dolomite	78.8	8.1	15.9	16.8	11.8	32.2
	calcite	4.1	-	0.5	1.1	-	0.9
	balance	8.6	2.6	5.0	3.5	2.8	7.8
Corresponding elemental composition %	Mg	12.3	25.6	23.7	23.8	25.4	20.5
	Ca	18.6	1.7	3.6	4.1	2.6	7.4
	Fe	0.87	1.81	1.73	1.73	1.25	1.36
	CO_3	59.4	68.2	65.9	66.8	67.9	63.1
	balance	8.8	2.7	5.1	3.6	2.8	7.6
Chemical analysis %	Mg	12.7	25.0	23.6	23.6	24.9	20.3
	Ca	17.9	1.65	3.30	3.30	2.44	7.75
	Fe	0.87	1.81	1.73	1.73	1.25	1.36
	CO_3	62.0	72.0	69.0	69.0	67.0	66.0
	balance	6.5	-0.5 [c]	2.4	2.4	4.4	4.6

a - = nil

b For convenience iron is reported as siderite although it is in solid solution

c Total exceeds 100%

TABLE 6

Weight Loss on Ignition of MAG 1 and XRD Intensity Ratios of Products[a]

Particle Size[b]	Temp. (°C)	Time (h)	LOI (%)	CaO/Dol	MgO/Dol
A	700	0.25	4.0	0	0
A	700	0.5	11.6	0.14	0.016
A	700	1.0	17.2	0.31	0.031
A	700	2.0	23.2	2.93	0.40
A	700	3.0	23.6	12.2	1.50
A	700	5.0	24.0	12.8	1.87
A	850	0.25	18.0	1.50	0.21
A	850	0.5	25.2	17.9	2.10
A	850	1.0	31.0	30.3	3.10
A	850	2.0	38.0	c	c
A	850	3.0	40.0	c	c
A	850	5.0	40.0	c	c
A	600	1.0	5.6	0	0
A	700	1.0	17.2	0.31	0.031
A	800	1.0	25.2	20	2.80
A	850	1.0	31.0	30.3	3.10
A	880	1.0	40.4	c	c
A	970	1.0	44.0	c	c
A	590	3.0	6.4	0.022	0.010
A	700	3.0	23.6	12.2	1.50
A	800	3.0	37.2	c	c
A	850	3.0	40.0	c	c
A	970	3.0	44.8	c	c
B	700	0.25	1.6	0	0
B	700	0.5	4.0	0	0
B	700	1.0	4.4	0.012	0.008
B	700	2.0	14.4	0.222	0.024
B	700	5.0	16.0	0.359	0.034
B	600	1.0	3.2	0	0
B	700	1.0	4.4	0.012	0.008
B	800	1.0	21.2	5.06	0.556
B	900	1.0	41.5	c	c

a Ratios of the intensities of the reflections of calcium oxide (CaO), dolomite (Dol) and magnesium oxide (MgO), [3.00, 2.886 and 1.489Å respectively]. The most intense reflection of magnesium oxide (2.106Å) was not used since it coincides with the second strongest reflection (2.102Å) of magnesite.

b A: $-\frac{1}{4}$" +7 mesh. B: $-\frac{1}{4}$" +7 mesh ground to 100% -100 mesh.

c No dolomite present.

TABLE 7

Weight Loss on Ignition of MAG 3 and XRD Intensity Ratios of Products[a]

Particle Size[b]	Temp. (°C)	Time (h)	LOI (%)	MgO/Mag	Mag/Dol
A	700	0.25	6.0	0	2.46
A	700	0.5	32.0	0.200	1.31
A	700	1.0	42.0	c	c
A	700	2.0	44.8	c	c
A	700	3.0	44.8	c	c
A	700	5.0	44.8	c	c
A	850	0.25	33.0	0.203	1.97
A	850	0.5	45.6	c	c
A	850	1.0	48.0	c	c
A	850	2.0	48.3	c	c
A	850	3.0	48.6	c	c
A	850	5.0	48.0	c	c
A	600	1.0	19.2	0.056	3.02
A	700	1.0	42.0	c	c
A	800	1.0	46.2	c	c
A	850	1.0	48.0	c	c
A	880	1.0	48.0	c	c
A	970	1.0	48.0	c	c
A	590	3.0	40.4	4.75	0.086
A	700	3.0	44.8	c	c
A	800	3.0	48.0	c	c
A	850	3.0	48.6	c	c
A	970	3.0	48.5	c	c
B	700	0.25	2.8	0	4.79
B	700	0.5	10.0	0.005	2.56
B	700	1.0	22.0	0.051	1.88
B	700	2.0	39.2	0.602	1.23
B	700	5.0	41.6	c	c
B	600	1.0	6.0	0.004	3.14
B	700	1.0	22.0	0.051	1.88
B	800	1.0	30.0	0.129	1.70
B	900	1.0	44.4	c	c

a Ratios of intensities of the reflections of magnesium oxide (MgO), magnesite (Mag) and dolomite (Dol), [1.489, 2.742 and 2.886Å respectively]. The most intense reflection of magnesium oxide (2.106Å) was not used since it coincides with the second strongest reflection (2.102Å) of magnesite.

b A: $-\frac{1}{4}$" +7 mesh. B: $-\frac{1}{4}$" +7 mesh ground to 100% -100 mesh.

c No magnesite present.

TABLE 8

Leach Test Data

Calcination conditions : 950°C/16 h
Pulp density : 2% solids (20 g/litre)
Agitation : 900 rpm

P_{CO_2} (psig)	50	75	100	100	100	100	125
Temp. (°C)	∿20[a]	∿20[a]	3.5	8.3	13.5	∿20[a]	∿20[a]
Time (h)	Soluble Mg^{++} (gpl)						
0.08	0.04			0.03		0.10	
0.13		0.04					
0.20			0.02				0.07
0.25					0.08		
0.33	0.09	0.08	0.04	0.04		0.12	
0.50			0.04	0.08	0.11		0.18
0.60	0.10	0.15				0.24	
0.75			0.08	0.16	0.20		0.23
0.90		0.21					
1.0			0.12	0.18			0.36
1.08	0.19					0.33	
1.25					0.30		
1.4		0.32					
1.5			0.16	0.24			0.51
1.6	0.34					0.53	
1.75					0.39		
1.9		0.45					
2.0			0.24	0.32			0.63
2.6	0.57					0.77	
2.75					0.60		
2.9		0.66					
3.0			0.33	0.46			0.87
3.6	0.74					1.00	
3.75					0.77		
3.9		0.88					
4.0			0.41	0.58			1.10
4.6	0.86					1.20	
4.75					0.91		

continued

TABLE 8 continued

Calcination conditions : 950°C/16 h
Pulp density : 2% solids (20 g/litre)
Agitation : 900 rpm

P_{CO_2} (psig)	50	75	100	100	100	100	125
Temp. (°C)	~20[a]	~20[a]	3.5	8.3	13.5	~20[a]	~20[a]
Time (h)	Soluble Mg^{++} (gpl)						
4.9		1.02					
5.0			0.50	0.73			1.25
5.6	0.95					1.34	
5.75					1.16		
5.9		1.20					
6.0			0.58	0.81			1.40
6.6	1.00					1.50	
6.75					1.20		
6.9		1.30					
7.0			0.61	0.90			
7.6	1.08					1.60	
7.75					1.32		
7.9		1.40					
8.0			0.67				
8.75					1.42		
9.75					1.50		
10.75					1.58		
11.75					1.63		
12.75					1.69		
13.75					1.78		
14.75					1.82		
17.75					1.95		
20.75					2.06		
23.75					2.11		

a In these tests, the temperature was not controlled but was allowed to increase slowly as the reaction proceeded.

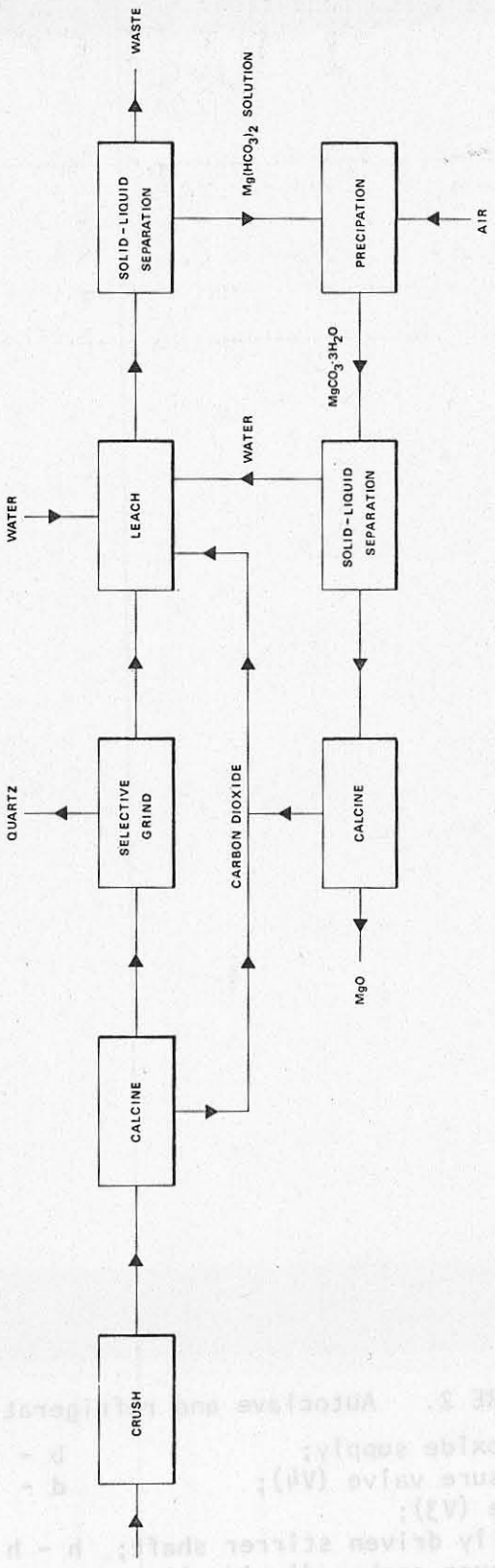

FIGURE 1. The carbon dioxide pressure leach process.

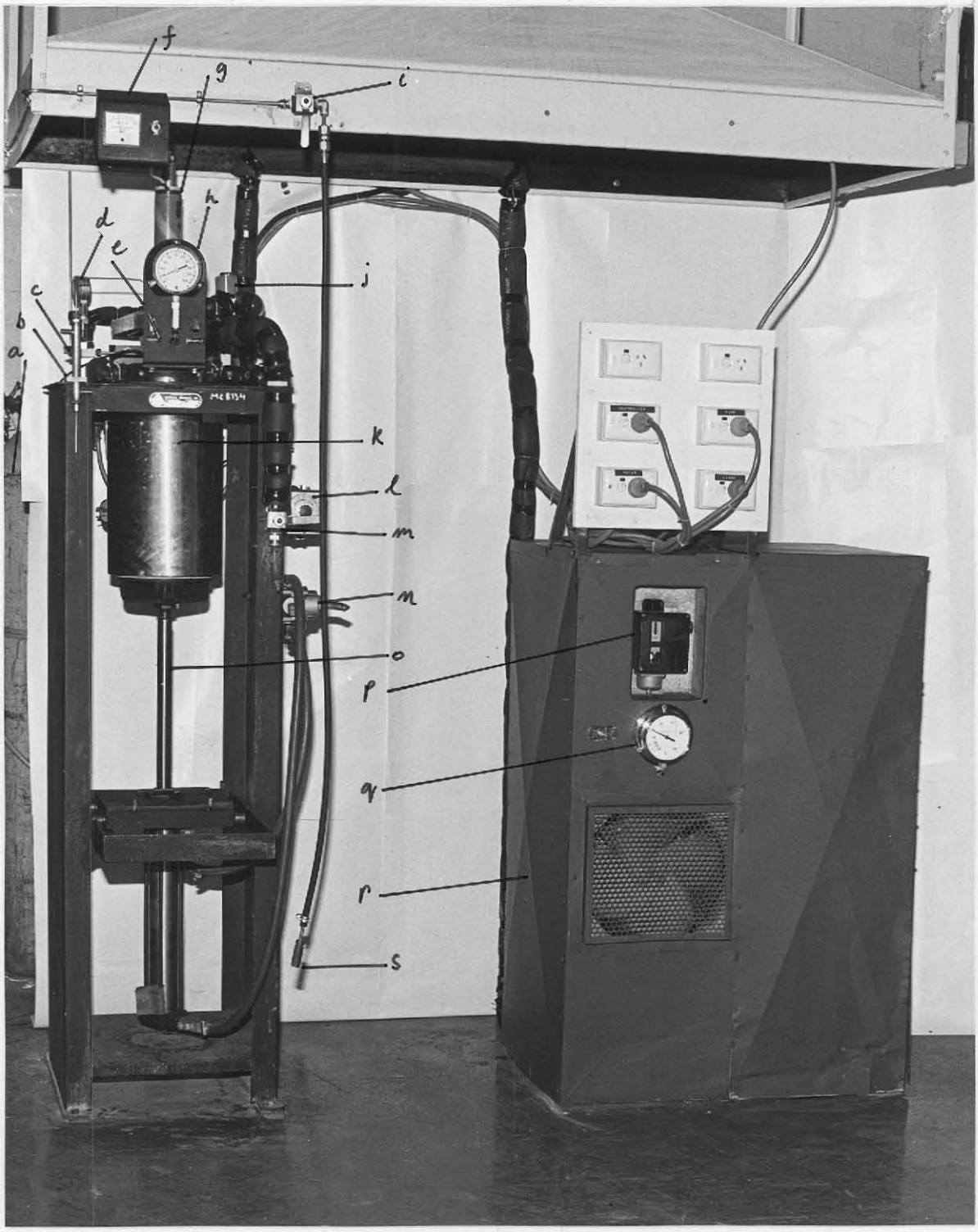

FIGURE 2. Autoclave and refrigeration system.

a - carbon dioxide supply; b - temperature sensor
c - high pressure valve (V4); d - low pressure gauge
e - vent valve (V3); f - tachometer
g - magnetically driven stirrer shaft; h - high pressure gauge
i - high pressure carbon dioxide line and valve (V1)
j - solenoid valve; k - autoclave inside insulation jacket
l - indicating temperature controller for autoclave
m - sampling tube and valve (V2); n - air leg controller
o - air leg; p - temperature controller (refrigeration unit)
q - gauge thermometer; r - refrigeration unit
s - flexible carbon dioxide supply for "blow back" via sampling tube and valve.

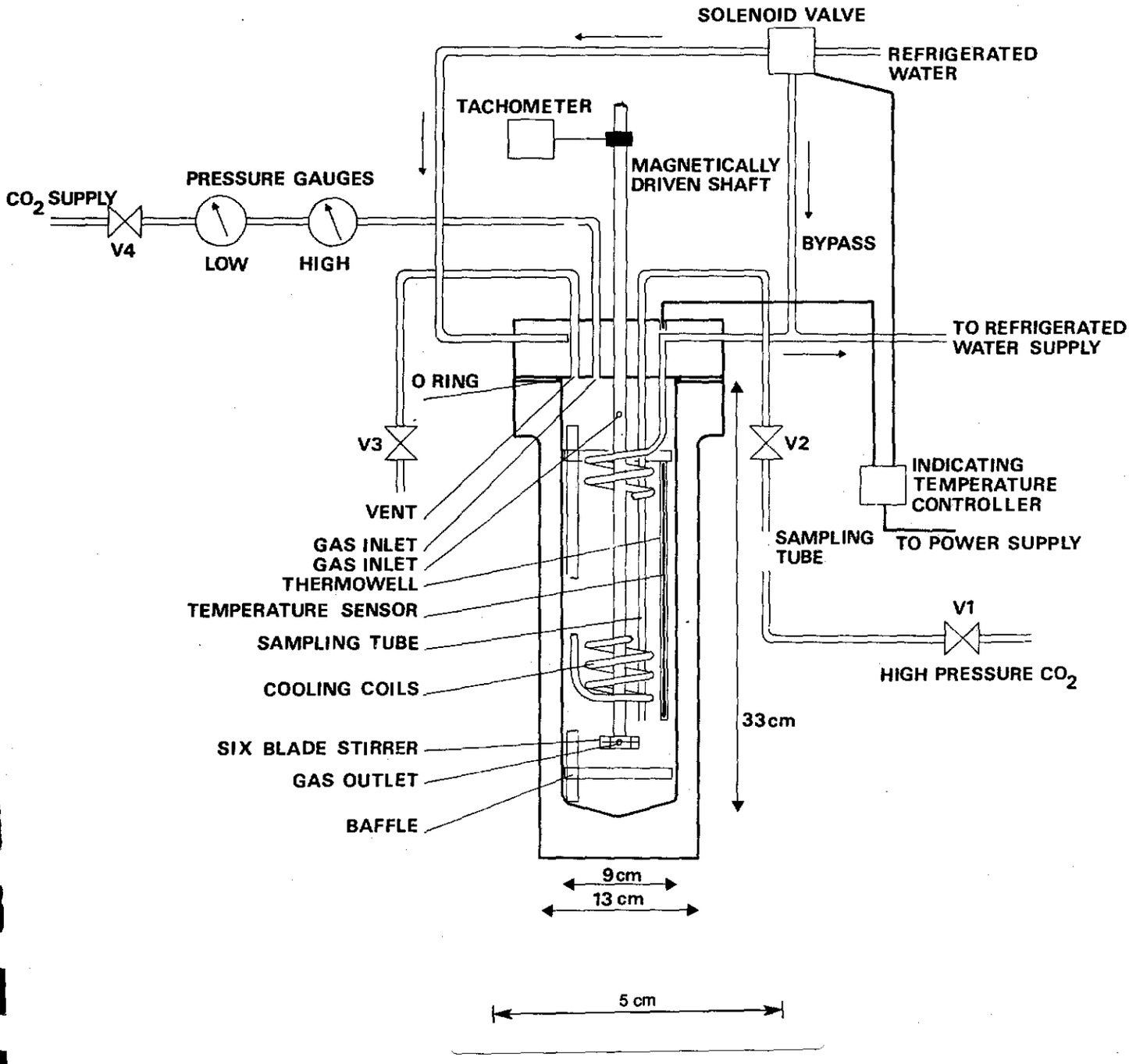

FIGURE 3. Details of autoclave and controls.

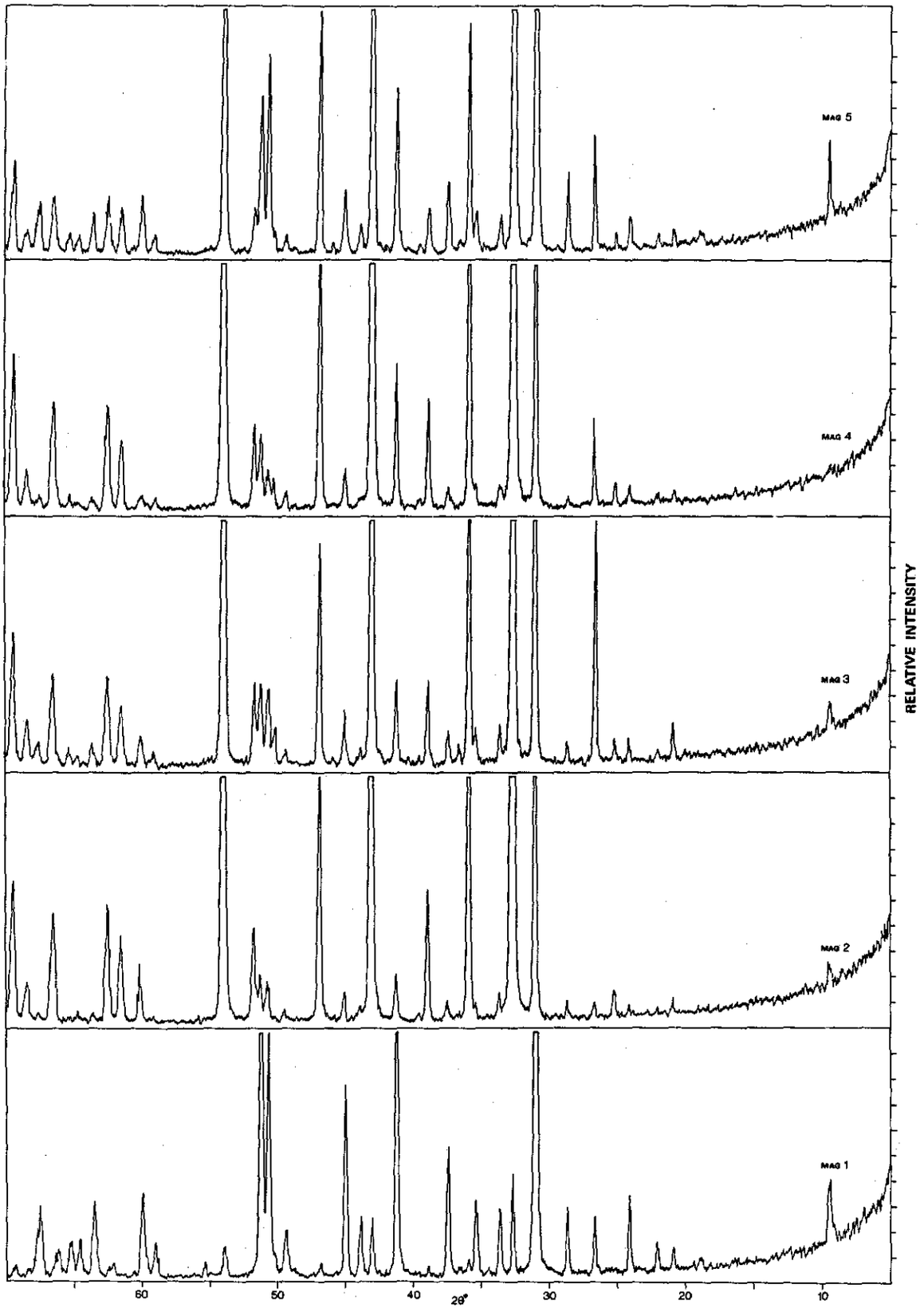

FIGURE 4. X-ray diffraction patterns of Savage River magnesite samples.

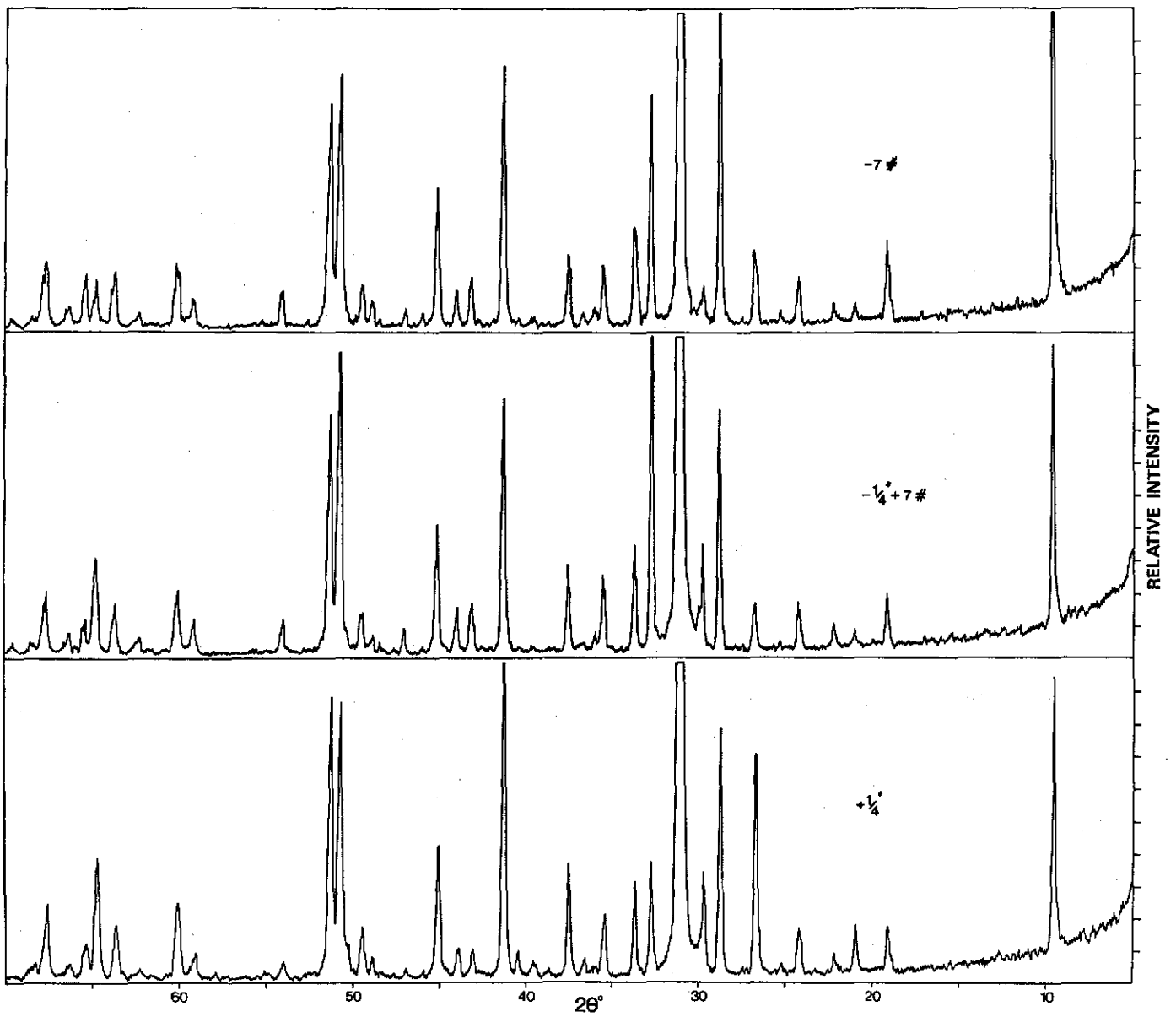

FIGURE 5. XRD patterns of MAG 1 as a function of particle size.

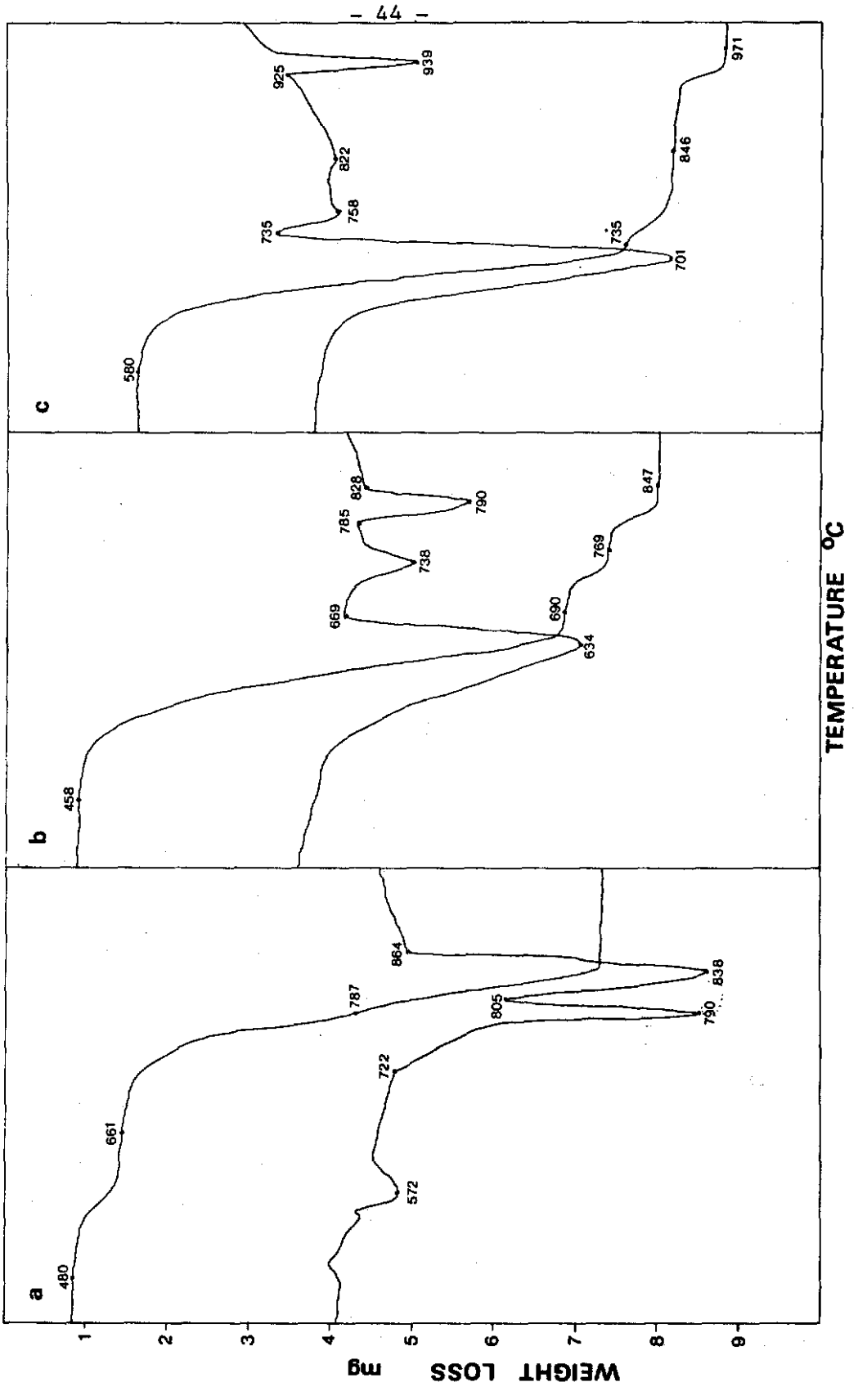

FIGURE 6. Differential thermal analysis and thermogravimetric analysis curves of MAG 1a (a), MAG 3a in air (b), and MAG 3a in flowing carbon dioxide (c). (Heating rate = 10°C/min).

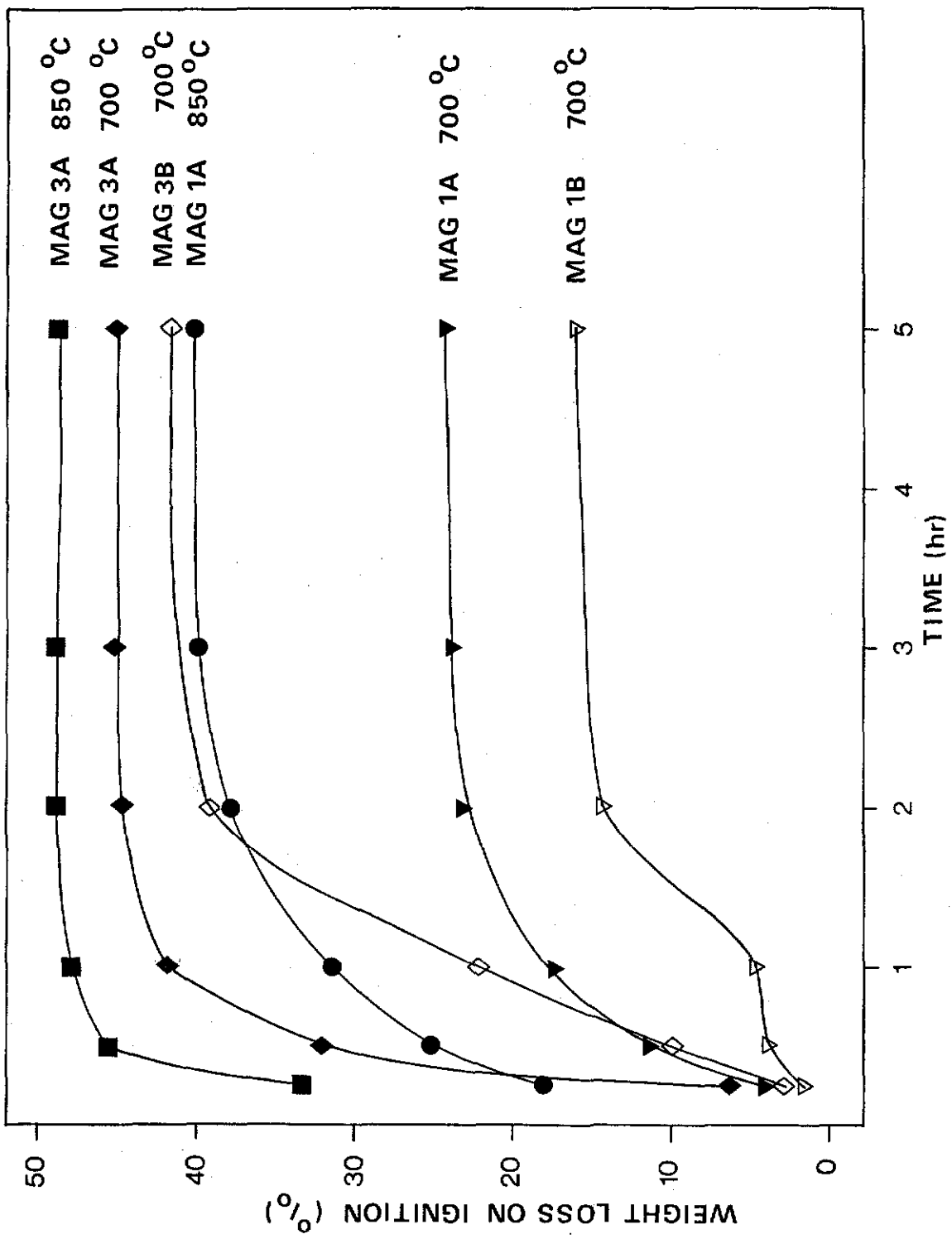

FIGURE 7. Weight loss on ignition as a function of time.
A = $-\frac{1}{4}$"+7 mesh, B = $-\frac{1}{4}$"+7 mesh ground to 100% -100 mesh.

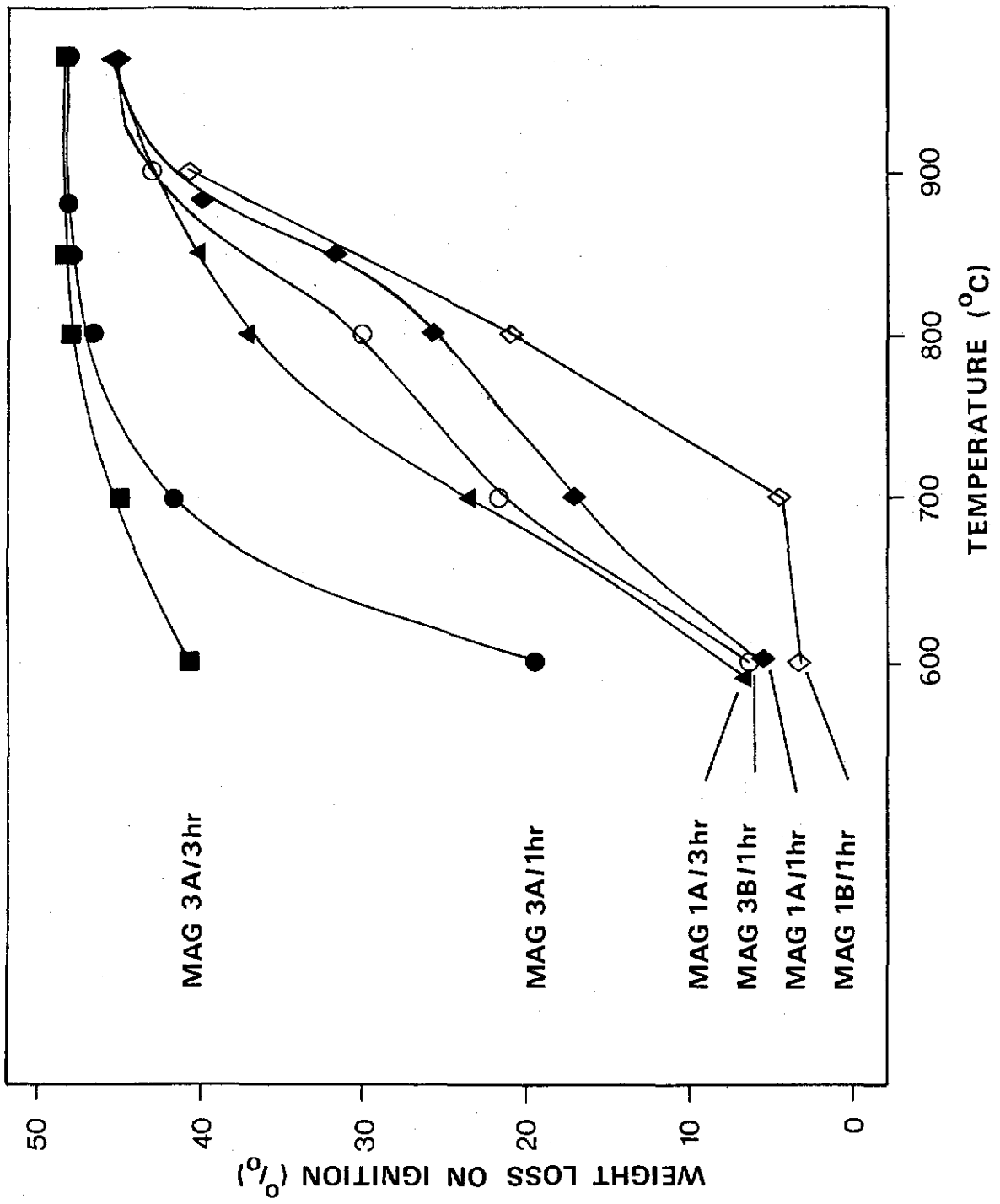

FIGURE 8. Weight loss on ignition as a function of temperature.
A = $-\frac{1}{4}$"+7 mesh, B = $-\frac{1}{4}$"+7 mesh ground to 100% -100 mesh.

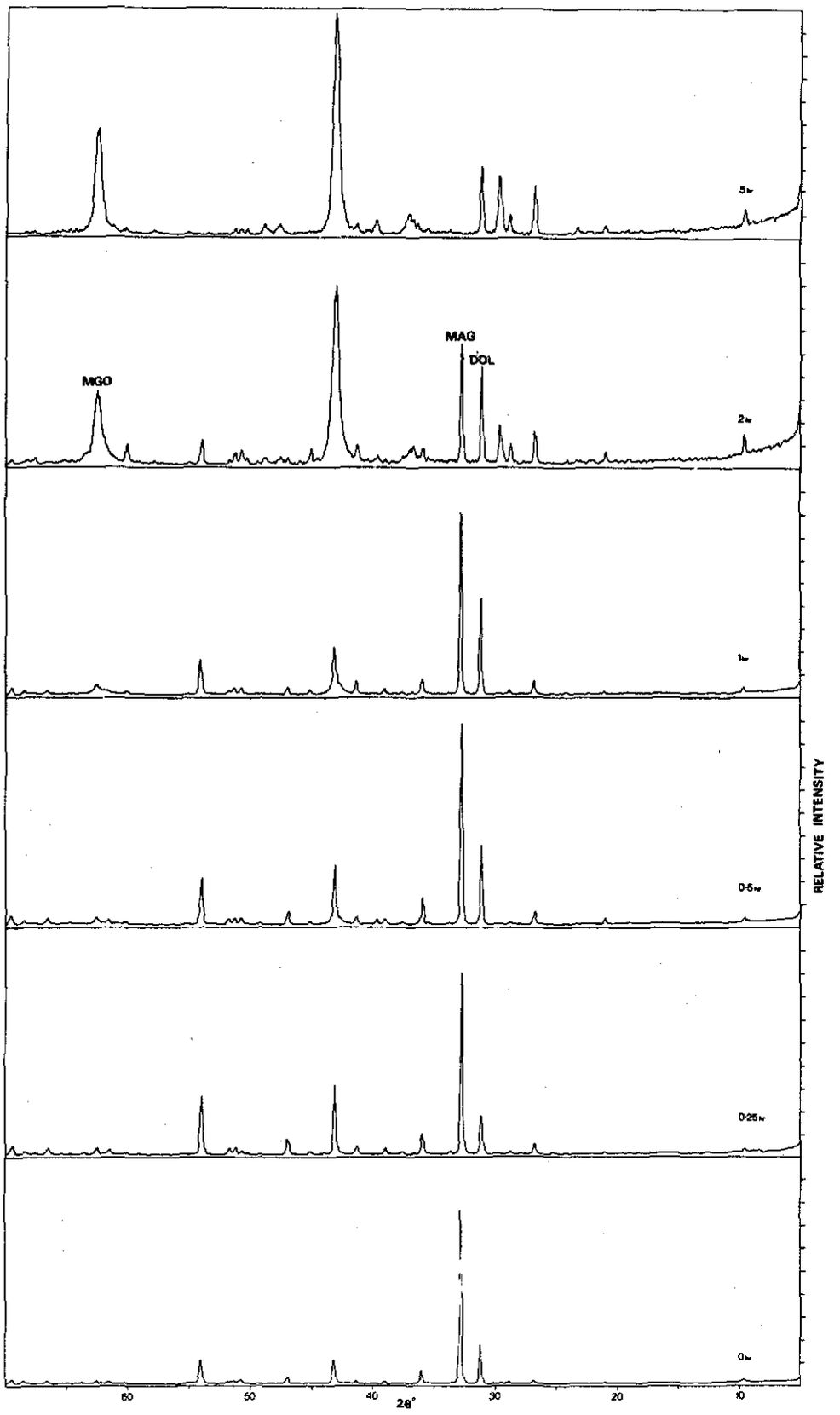

FIGURE 9. XRD patterns of MAG 1 (-¼"+7 mesh ground to -100 mesh) calcined at 700°C - effect of time of calcination.

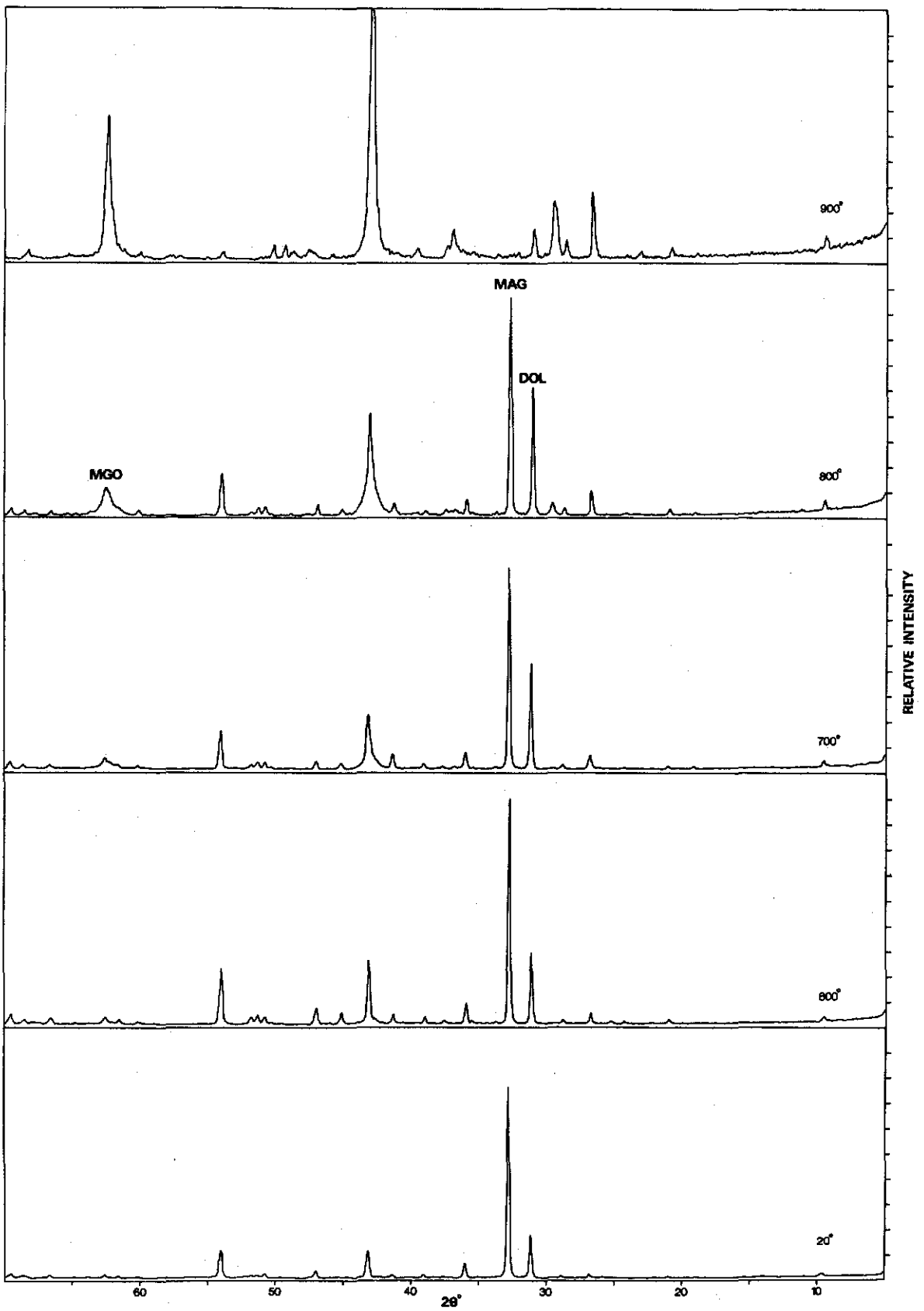

FIGURE 10. XRD patterns of MAG 1 ($-\frac{1}{4}$"+7 mesh ground to -100 mesh) calcined for 1 hour - effect of temperature of calcination.

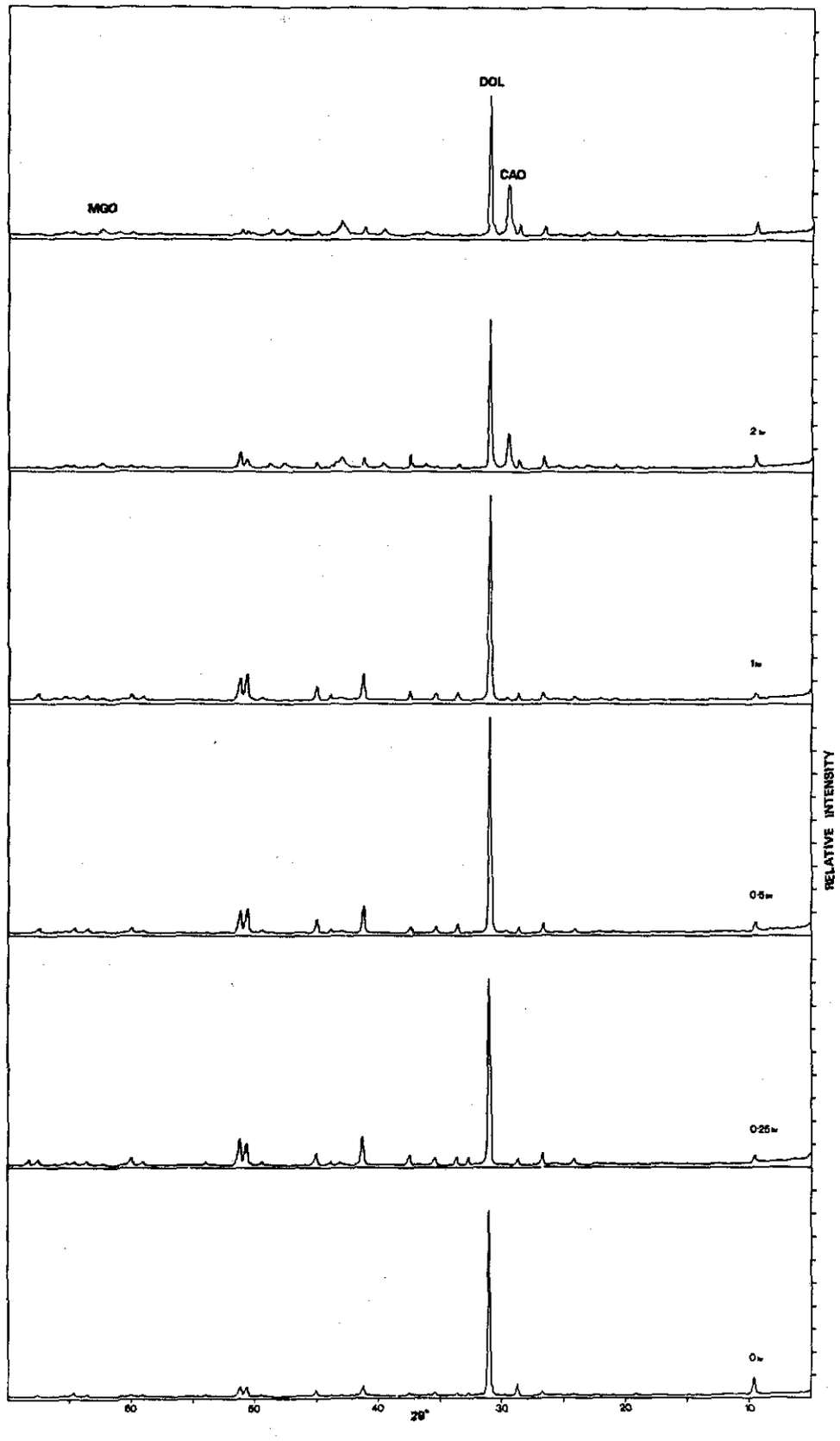

FIGURE 11. XRD patterns of MAG 3 (-¼"+7 mesh ground to -100 mesh) calcined at 700°C - effect of time of calcination.

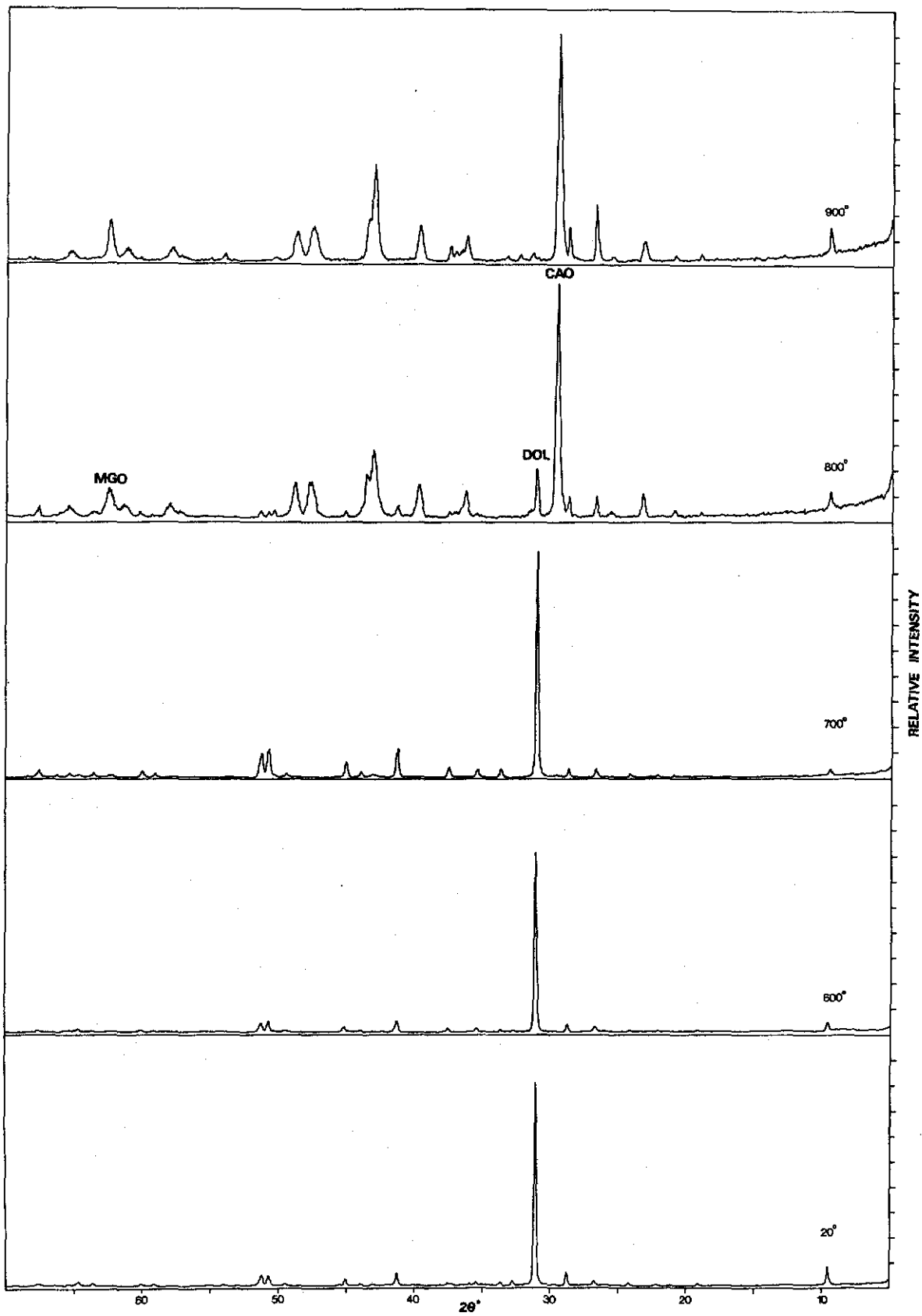

FIGURE 12. XRD patterns of MAG 3 (-¼"+7 mesh ground to -100 mesh) calcined for 1 hour - effect of temperature on calcination.

FIGURE 13. MAG 3 prior to calcination (*left*) and after heating to 900°C for 1 hour (*right*). Note white particles present in calcine.

FIGURE 14. Particle of calcined MAG 3 showing development of cracks due to change in volume on evolution of carbon dioxide.

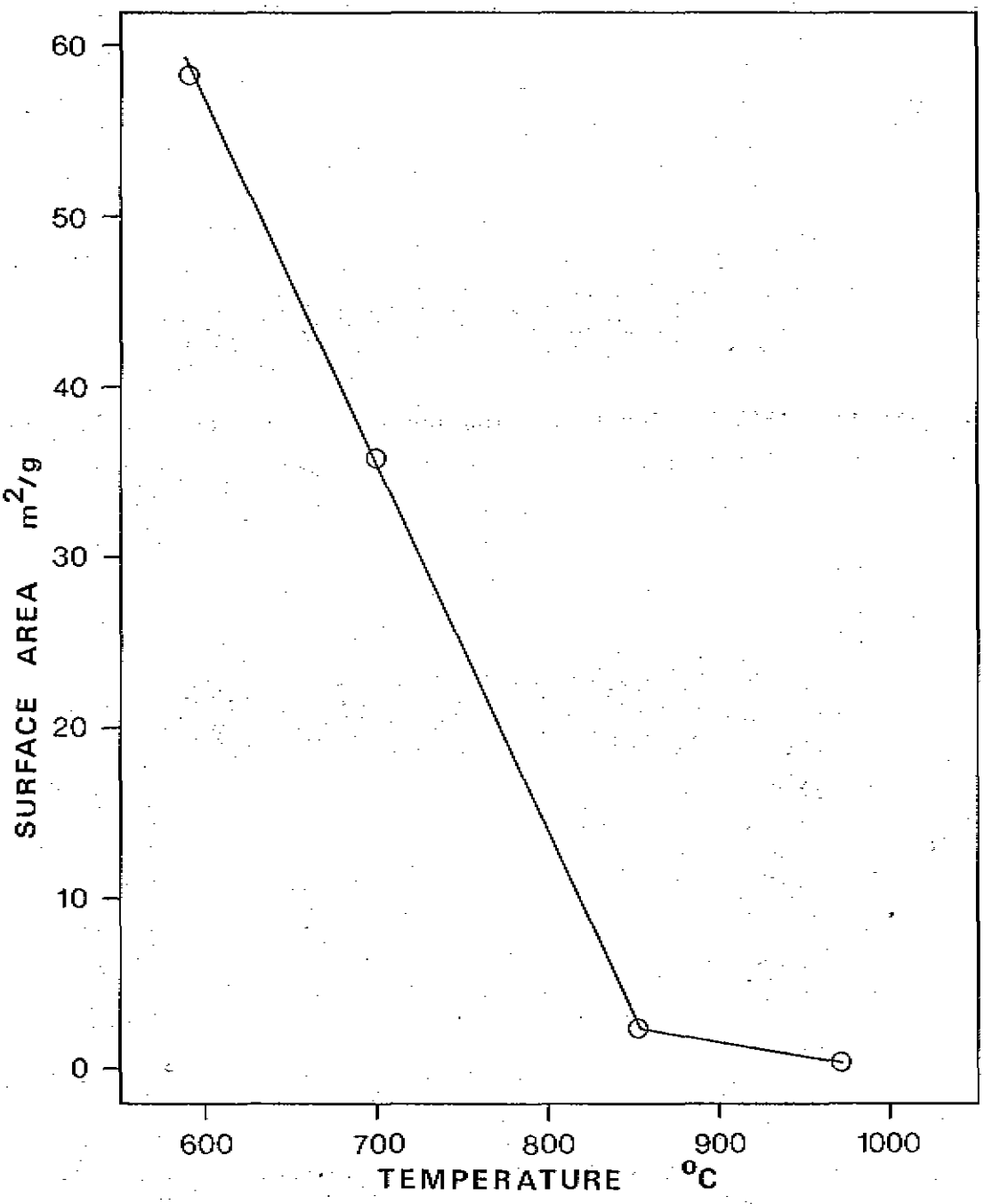

FIGURE 15. Surface area of calcine formed from MAG 3 (-¼"+7 mesh ground to -100 mesh) as a function of calcination temperature.

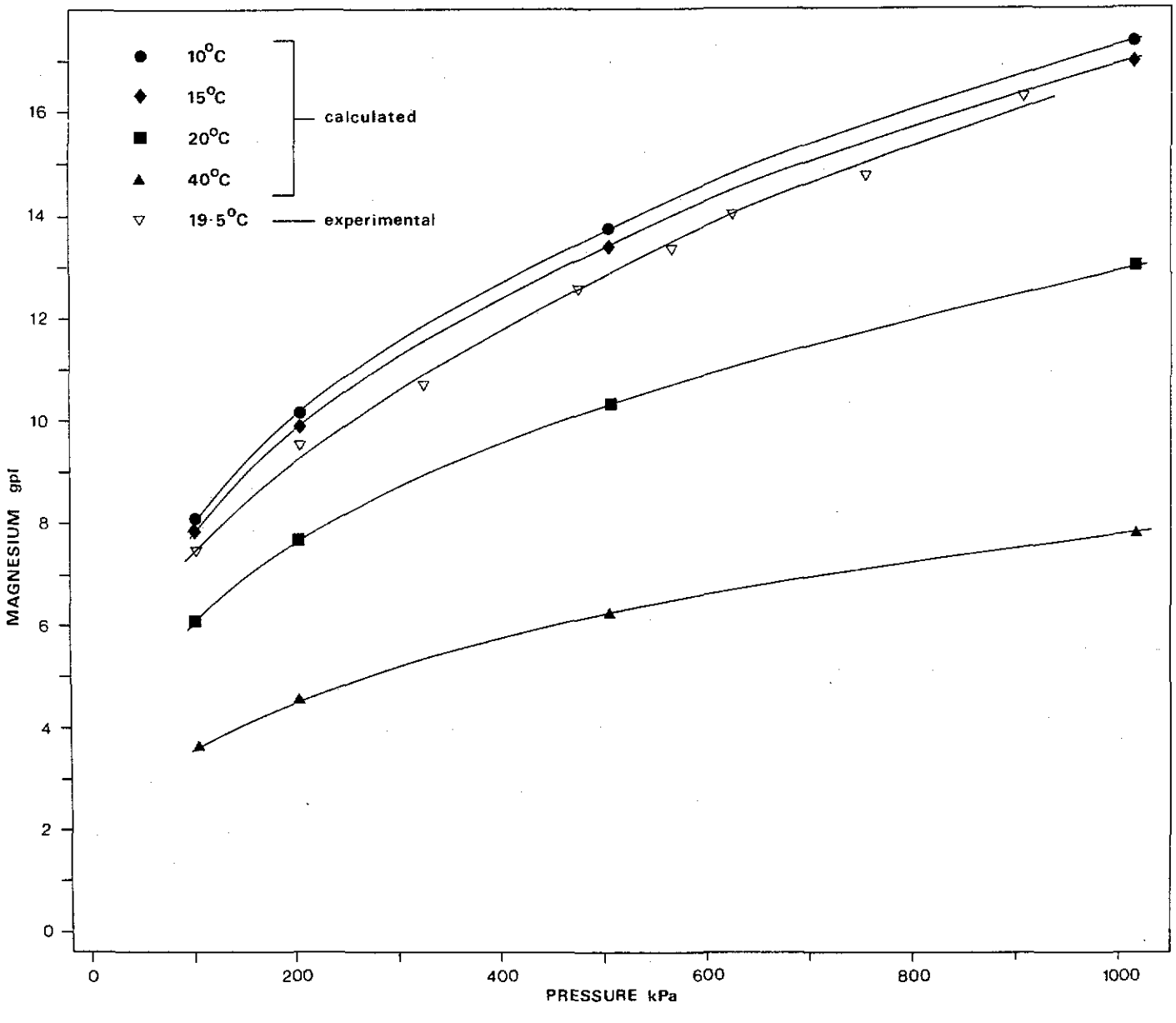

FIGURE 16. Solubility of magnesium carbonate as a function of temperature and carbon dioxide partial pressure.

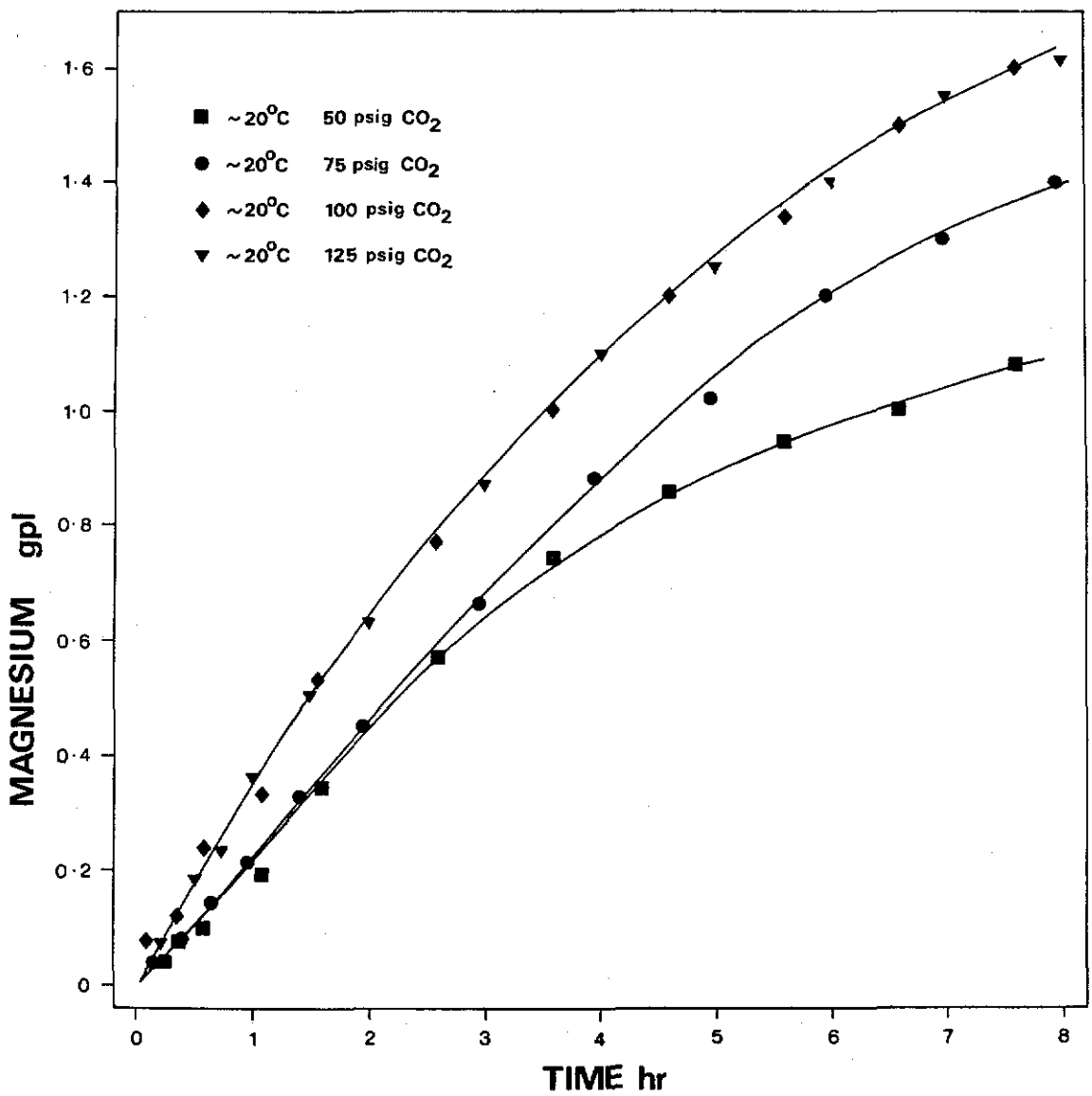

FIGURE 17. Solubility of magnesium as a function of time and carbon dioxide partial pressure. Calcination conditions: 950°C/16 h.

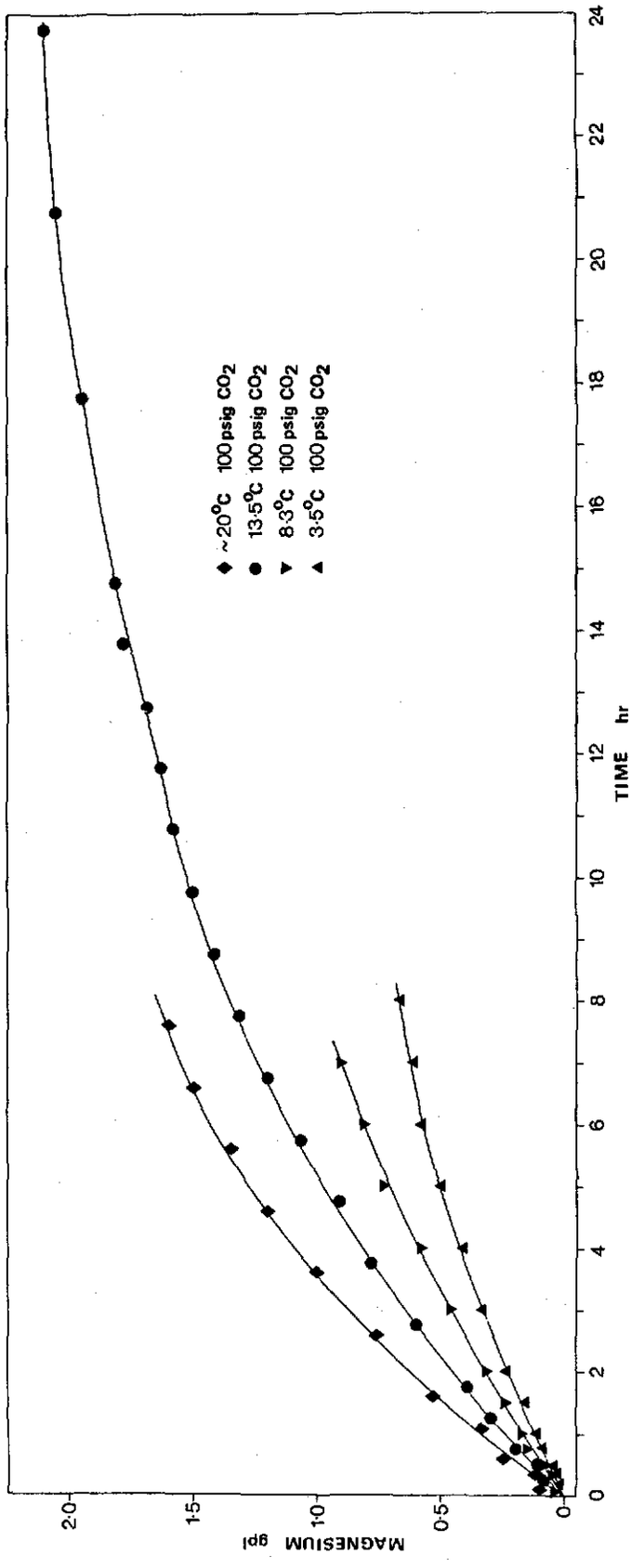

FIGURE 18. Solubility of magnesium as a function of time and temperature.
Calcination conditions: 950°C/16 h.

C S I R O

IRR 1053

INSTITUTE OF EARTH RESOURCES
DIVISION OF MINERAL CHEMISTRY

PRODUCTION OF MAGNESIA FROM SAVAGE RIVER MAGNESITE

by

J.H. CANTERFORD and P.T. EVERSON

Report No. 2 ======= June-August, 1979

Division of Mineral Chemistry
P.O. Box 124, Port Melbourne
Victoria 3207

September 1979

CONTENTS

SUMMARY

The present report is mainly concerned with the influence of calcination and leaching conditions on the recovery of magnesium from sample MAG 3. Calcination temperature, and to a lesser extent time, has a marked influence on leaching kinetics and the degree of magnesium dissolution. For this sample, optimum calcination conditions are at 700°C for one hour. Analytical, X-ray diffraction and thermogravimetric data indicate that other samples of Savage River magnesite are likely to have significantly different optimum calcination conditions. Changes in leaching conditions - temperature, slake conditions, pulp density, carbon dioxide partial pressure, agitation - have a small effect on the kinetics and degree of magnesium dissolution. However, these changes have a pronounced effect on the amount of iron simultaneously dissolved. Pregnant liquors with low iron contents are produced with low pulp densities and carbon dioxide pressures and at elevated temperatures.

The product formed from clarified leach liquors depends on the temperature of precipitation. The two main products have quite different physical and chemical properties. Both yield magnesium oxide, the desired product, on calcination at relatively low temperatures (∿ 600°C). To produce a product acceptable to the market, calcination at much higher temperatures (1000-2000°C) is required.

On the basis of experimental data obtained to date and consideration of engineering principles, a flowsheet for the calcination/carbon dioxide pressure leach process is described.

The report concludes with a section on the proposed testwork programme for the next quarter.

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INTRODUCTION

In the previous report (1) the methods of production of magnesium oxide were reviewed, and on the basis of the known chemical and mineralogical properties of Savage River magnesite samples then available, it was concluded that a chemical dissolution technique rather than physical beneficiation was the appropriate magnesium oxide recovery route for this ore. Several chemical dissolution techniques have been reported in the literature; of these calcination/carbon dioxide pressure leaching appears to be superior and the present series of quarterly reports detail the results obtained when this production route is applied to Savage River magnesite.

In the previous quarter the experimental work was principally concerned with the chemical and mineralogical characterization of the five magnesite samples provided, detailed muffle calcination tests for weight loss determination and the provision of suitable samples for leaching tests, characterization of calcines, and the carrying out of a limited number of pressure leach tests. The following conclusions were drawn from the results.

- X-ray diffraction readily indicates the dolomite to magnesite ratio of each ore sample and can be used to qualitatively determine the heating profile to which each calcine has been subjected.

- The ore should be crushed to a small enough size to permit even yet complete calcination. Heat transfer and solid flow properties during calcination would also influence the optimum ore size.

- On calcination there is a reduction in weight and bulk volume of about 50% and 10% respectively. During calcination there is also a marked reduction both in particle size and hardness. These factors indicate that grinding to a suitable particle size for leaching would be carried out most economically after calcination.

- Any quartz present in the ore can be removed by selective grinding and screening of the calcine. This reduces the

overall load on the grinding circuit as well as reducing the amount of solids that have to be removed from the pregnant leach slurry.

- Dolomite is thermally more stable than magnesite. Moreover, the temperature required to decompose the magnesium carbonate content of the dolomite is greater than that of the magnesium carbonate present as magnesite.

- Surface area and hence chemical reactivity are dependent upon the time and temperature of calcination. To obtain a reactive product it appears that a lower temperature but longer time is, in general, more appropriate than a higher temperature for a shorter time.

- To ensure that the calcine has a suitably high chemical reactivity for leaching, it would be advantageous to keep the dolomite content of the ore as low as possible. This would increase the proportion of the leach feed which would be dissolved and thus decrease the amount of unreacted residue that has to be removed from the pregnant leach slurry.

- It is advantageous to remove the carbon dioxide from the atmosphere surrounding the ore during calcination since this lowers the temperature necessary for "complete" dissolution. However, as the carbon dioxide is to be recovered and used in the leaching stage, it should not be diluted too much.

- The kinetics of the dissolution of the magnesium oxide component of the calcine are markedly dependent on the calcination conditions.

- For high temperature (950^{o}C) calcines, leaching at room temperature with a moderate carbon dioxide pressure is more appropriate than at a lower temperature even though the solubility of magnesium carbonate is higher at the lower temperature.

- For low temperature (700^{o}C) calcines, it is possible to dissolve about 90% of the available magnesium in a relatively short time yielding a solution which approaches saturation with respect to magnesium carbonate.

The present report is principally concerned with detailed kinetic studies of the dissolution of the magnesium oxide component of calcines formed under different conditions. These studies were carried out in order to assess the effects of calcination time and temperature, pulp density, slake conditions, leach liquor composition, carbon dioxide partial pressure and temperature on the amount of magnesium and iron dissolved as a function of leaching time. Associated with these studies were the recovery and characterization of intermediate and final products from clarified pregnant liquors and testing of the technical scale rotary kiln.

While the above experimental programme was being carried out, it became quite apparent that before the technical scale test work could be logically planned and carried out, it was essential that detailed consideration be given to process design factors. The calcination, leaching and product quality data derived from the experimental programme were used to develop a possible overall flowsheet.

Several workers (2-5) have shown that it is possible to leach calcined magnesite with carbon dioxide at atmospheric pressure, that is, using a flow of carbon dioxide. Although it was previously considered that pressure leaching was more appropriate than leaching at atmospheric pressure (1), it was decided that it would be appropriate to carry out a limited number of atmospheric pressure leach tests. The results of the first of these tests are presented in this report.

EXPERIMENTAL

ROTARY KILN

A technical scale rotary kiln (Figure 1) was available for calcination of suitable quantities of ore prior to carbon dioxide pressure leaching in the technical scale autoclave rig. The kiln consists of a 2.5 m × 0.1 m stainless steel (25/20) tube rotated by a variable speed drive with a gas inlet for purging and is indirectly heated via a three-section tube furnace with a

maximum operating temperature of 950°C. Approximately 1.5 m of the kiln could be heated and maintained at the operating temperature. The ore is introduced into the kiln by means of a variable speed screw feeder. Because of limitations imposed by the size of the screw feeder, the ore has to be crushed to -¼". The retention time is determined by the ore particle size range, feed rate, rotation and angle of inclination. The temperatures of the three separate heating elements are controlled by Pyrotenax thermocouples which can be inserted between the stainless steel tube and the alumina tube on which the heating elements are wound, or inserted into the bed of solid moving down the tube.

Test runs were carried out with bricklayers sand and indicated that about three hours were required for a steady state flow (about 4 kg/h) to be reached. For a bed temperature of 700°C, a heat-up period of approximately one hour was required, and it was necessary to maintain a winding temperature of 730°C.

Because of the limited amount of magnesite ore available, calcination of ore has, as yet, to be carried out in this technical scale rotary kiln. Because of the endothermic nature of the calcination reactions (1), a significant temperature differential between bed and windings would be expected.

PRESSURE LEACHING

The pressure leach kinetic runs were carried out as previously described (1) with the exception that the blow back carbon dioxide pressure used to prevent blockage of the sampling tube and valve was limited to 5 psig rather than 25 psig above the operating pressure. Unless otherwise noted, each test run commenced with a 0.5 h slaking period at the operating temperature during which time the autoclave was sealed.

ATMOSPHERIC PRESSURE LEACHING

Leaching was carried out in a one litre Pyrex reaction vessel equipped with a variable speed stirrer, a thermometer,

condenser and vent, carbon dioxide inlet fitted with a number 1 porosity sinter, and a sampling port. The carbon dioxide was added via a calibrated flow meter; for the single test reported here a flow rate of 5 ℓ/min was used. In this test no attempt was made to operate at a constant temperature; such constant temperature runs would be readily carried out in a suitably regulated constant temperature bath.

OTHER EXPERIMENTAL TECHNIQUES

Chemical and mineralogical analyses, muffle calcination tests, etc., were carried out as previously described (1).

RESULTS AND DISCUSSION

MUFFLE CALCINATION TESTS

The calcines derived from the muffle calcination tests were previously characterized by X-ray diffraction analysis (1). The diffraction patterns of the calcines gave some indication of the temperature profile to which they had been subjected, but to allow a more complete characterization, each of the calcines was chemically analysed. As complete as possible characterization is considered essential, particularly for the products of the technical scale rotary kiln since it would not be accurately known beforehand to what time and temperature each sample had been subjected. The chemical analyses were also necessary for calculation of magnesium extraction on leaching in order to determine optimum calcination conditions.

Tables 1 and 2 give the magnesium, calcium and iron contents of the calcines derived from the -¼"+7 mesh fractions of samples MAG 1 and MAG 3. The analyses are consistent with the weight loss on ignition and X-ray diffraction data reported previously (1).

In the present quarter all of the optimization pressure leach tests were carried out on a bulk sample of the -¼"+7 mesh fraction of MAG 3 calcined in the muffle furnace at 700°C for 3 h.

The calcine was ground to 100% -100 mesh after calcination and three separate grab samples of the bulk sample yielded the following chemical analyses (%):

	Mg	Ca	Fe
	38.7	5.31	2.94
	39.7	5.32	2.93
	39.0	5.22	2.86
Average	39.1	5.28	2.91

Dry screening gave the following particle size distribution:

-100+150 mesh	3.7%
-150+200 mesh	8.1%
-200+300 mesh	6.6%
-300 mesh	81.6%

X-ray diffraction analysis indicated that the bulk sample was mainly magnesium oxide (∿ 90%) with smaller amounts of magnesite, dolomite, calcite and quartz. There was no evidence for iron oxide. The above mineralogical assemblage was confirmed by conventional optical microscopy. It was noted, however, that the magnesium oxide, which was present as small clear particles, was stained yellow - presumably by iron oxide. This is consistent with the already established fact that the iron is present in the magnesite by lattice substitution. The presence of a small amount of undecomposed magnesite in the 700°C/3 h bulk calcine is also consistent with the expected chemical composition of completely decomposed MAG 3.

LEACHING OF CALCINES - GENERAL COMMENTS

Considering only the magnesium oxide component of the calcine, the two principal reactions proceeding during leaching are:

$$MgO + 2CO_2(g) + H_2O \longrightarrow Mg^{++}(aq) + 2HCO_3^-(aq) \qquad (i)$$

$$MgO + H_2O \longrightarrow Mg(OH)_2 \qquad (ii)$$

Reaction (i) probably involves two separate steps:

$$MgO + CO_2(g) + xH_2O \longrightarrow MgCO_3 \cdot xH_2O \qquad \text{(iii)}$$

$$MgCO_3 \cdot xH_2O + CO_2(g) \longrightarrow Mg^{++}(aq) + 2HCO_3^-(aq) \qquad \text{(iv)}$$

Reaction (ii) is the normal slaking reaction of alkaline earth oxides. Magnesium bicarbonate is only stable in solution in the presence of excess carbon dioxide; once the carbon dioxide pressure is reduced, hydrated magnesium carbonate or a basic magnesium carbonate is precipitated.

Calcium and iron oxides are considerably less reactive than magnesium oxide; little is known about the reactions but they are possibly

$$CaO + 2CO_2(g) + H_2O \longrightarrow Ca^{++}(aq) + 2HCO_3^-(aq) \qquad \text{(v)}$$

$$Fe_2O_3 + 3CO_2(g) + H_2O \longrightarrow 2Fe^{++}(aq) + 3CO_3^{=}(aq) \qquad \text{(vi)}$$

The iron and calcium contents of the final product of the overall process, MgO, have an influence on its use and value. In general, the lower the impurity level, the greater the value. The aim of the present project is to develop a process for producing high grade magnesium oxide, and so the extent to which reactions (v) and (vi) proceed is critical. From literature data it was initially believed that conditions could be readily established under which reactions (v) and (vi) did not proceed to any significant extent. However, it quickly became apparent that for calcines derived from MAG 3, reaction (vi) did in fact occur at an appreciable level for quite a wide range of leaching conditions. Thus the clarified pregnant liquors were often a distinct rust red-brown colour and contained up to 330 ppm iron. On standing open to the atmosphere the carbon dioxide content of the liquors decreased slowly over several hours to such an extent that reaction (vi) was reversed and iron oxide (hematite) precipitated on the surfaces of the hydrated magnesium carbonate that also precipitated on standing. Thus, in order to obtain an accurate estimation of the amount of iron dissolved, it was essential that the sample liquors be analysed as soon as possible after collection.

With calcines derived from sample MAG 3, analysis of clarified pregnant leach liquors yielded calcium contents of less than 10 ppm indicating that reaction (v) did not proceed to any significant extent. For calcines derived from MAG 1, which have higher calcium contents than those from MAG 3 (see Tables 1 and 2), reaction (v) may become more significant with respect to product purity.

For a given calcine, the rates at which reactions (ii) - (vi) proceed depend upon

slaking time and temperature
pulp density
temperature
carbon dioxide partial pressure
leach liquor composition
agitation

Previously (1) it was shown that the rate of magnesium oxide carbonation [reactions (iii) and (iv)] is also dependent upon the temperature and time of the preceding calcination step; this could be related to the surface area of the calcine. Surface area and hence reactivity decrease rapidly on increasing the calcination temperature from 700°C to 970°C. An increase in calcination time at a low temperature (700°C) has only a marginal effect on surface area; at higher temperatures ($\geq$ 850°C) there is a more pronounced decrease in surface area as the calcination time is increased. The extent of calcination, that is, the conversion of magnesium carbonate to magnesium oxide, also has to be taken into account. Calcination is an energy intensive unit process so that optimum calcination conditions must be determined with respect to reactivity, magnesium carbonate conversion and energy requirements.

PRESSURE LEACH TESTS - BULK CALCINES

Previous experience in these laboratories has shown that with an autoclave of the type used in the present study, an impeller fitted with a Snyder sub-aerator and rotated at 900 rpm would ensure that the solids would remain in suspension and that there would be adequate gas/liquid mixing. Tests confirmed that over the range of

pulp densities used there was sufficient agitation to keep the solids in suspension and gas/liquid mixing appeared adequate. Thus for virtually all leach tests the impeller was rotated at 900 rpm. Towards the end of the quarter, the influence of a higher rotational speed was investigated and it was found that there was a marked difference in the form of the leaching curves. This finding means that some of the conclusions presented in this report require a limited amount of modification for the case where a higher (> 900 rpm) agitation speed is considered.

The leaching data obtained with an impeller rotation of 900 rpm are given in Tables 3-7 and Figures 2-12 and 14. It is to be noted that most of the leaching curves do not have the normal form expected for a reaction between a simple solid and a gas dispersed throughout the slurry. In most cases there appears to be two or more leaching stages and this phenomenon can probably be attributed to the formation of intermediate products such as a hydrated magnesium carbonate

$$MgO + CO_2(g) + xH_2O \longrightarrow MgCO_3 \cdot xH_2O$$

or a basic carbonate such as hydromagnesite

$$5MgO + 4CO_2(g) + 5H_2O \longrightarrow Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O \qquad \text{(vii)}$$

In a number of kinetic runs precipitation had obviously taken place during the initial stages of the run. Several of these precipitates were collected during sampling and their X-ray diffraction patterns recorded. These patterns were generally ill-defined, consisting of two broad reflections at about 5.2 Å and 2.6 Å, a number of less intense reflections, as well as the reflections of unreacted magnesium oxide. The identity of the precipitates could not be positively determined from the diffraction patterns. Similar precipitates were also observed in the leach residues remaining after completion of kinetic runs in which the magnesium bicarbonate solubility limit had been exceeded.

Reproducibility

Figure 2 shows the kinetic data for three test runs carried out under identical conditions; there is a small but not unreasonable scatter in the data. It is quite apparent that the experimental techniques used provide reliable kinetic data.

Effect of Slake Time and Temperature

From Figures 3-5 and Tables 3 and 4, it can be clearly seen that both increases in slake time and slake temperature have no significant effect on the total magnesium extraction once reaction has gone to completion, even though, in some cases, the actual kinetics of magnesium oxide dissolution are improved. However, such increases in slake time and slake temperature lead to marked increases in the amount of iron dissolved. Excessive iron dissolution would, of course, result in the recovery of intermediate and final products with iron contents which exceed market specification.

During the slaking period some of the magnesium oxide is converted to magnesium hydroxide.

$$MgO + H_2O \longrightarrow Mg(OH)_2 \qquad \text{(ii)}$$

Both the magnesium hydroxide and the unreacted magnesium oxide react with the carbon dioxide once the latter is added. There is no comparable chemical reaction for iron oxide, so the chemical formation of an intermediate which has a higher reactivity with respect to reaction with carbon dioxide can be discounted. During slaking it is possible that the physical properties of the iron oxide are altered in some way, producing the observed higher reactivity once carbon dioxide is added.

Wet or dry milling is to be used to reduce the particle size of the calcine to a level suitable for leaching. It is quite apparent from the above discussion that wet milling must be carried out as quickly as possible at a temperature at or close to ambient in order to limit the amount of iron dissolved.

Effect of Pulp Density

At a leaching temperature of 15.5°C and a carbon dioxide pressure of 100 psig, increasing the pulp density from 2% solids to 5% solids has no effect on the percentage of magnesium extracted at the completion of each kinetic run (see Tables 3 and 5 and Figure 6). However, there are notable differences in the kinetics of magnesium oxide dissolution, with precipitation of an intermediate basic magnesium carbonate during the first 1-1¼ hours leaching at 4% and 5% solids. More importantly, the amount of iron dissolved increases rapidly as the pulp density is increased; the amount of iron dissolved as a percentage of the magnesium dissolved increases from 0.23% to 1.09% when the pulp density is increased from 2% to 5% solids.

When the leaching temperature is increased to 30°C, the influence of an increase in pulp density is more complex because the solubility limit of magnesium bicarbonate is reached at the higher pulp densities (see Tables 3 and 5 and Figure 7). On increasing the pulp density from 2% to 3% solids there is a significant decrease in the percentage of magnesium dissolved from 84% to 79% to 70%. The proportion of iron extracted increases as the pulp density is increased, but it is to be noted that it is significantly less than at the comparable pulp density at 15.5°C.

On a batch leaching basis, as carried out here, it is obvious that although the time required to achieve complete magnesium oxide dissolution increases as the pulp density increases, a higher total amount of magnesium solubilized is achieved at the higher pulp densities. Thus Figure 6 shows that 13 g of soluble magnesium are formed in approximately 2.25 h at a pulp density of 4% solids. At 2% solids, about 3.5 h would be required to achieve the same quantity of soluble magnesium; moreover, two separate batch leaching stages would be required.

The precipitation of basic magnesium carbonate that becomes pronounced as the pulp density is increased could cause problems when leaching is carried out on a continuous basis. It

has been established (2) that an excess of magnesium oxide in the reaction mixture can result in the reversal or stoppage of the dissolution reactions noted previously by interaction of the magnesium oxide with the soluble magnesium bicarbonate and/or any precipitated basic magnesium carbonate.

From a process point of view, it is obviously advantageous to leach at as high a pulp density as possible since this increases plant capacity. In the calcination/carbon dioxide pressure leach process the maximum practical pulp density is partially determined by the solubility limits of magnesium bicarbonate, partially by the level of iron dissolution that can be tolerated, and partially by the importance of the dissolution reaction reversal by excess magnesium oxide. From the above results it is clear that the leaching temperature controls the solubility limit and the degree of iron dissolution and thus has a major influence on the maximum practical pulp density.

Effect of Leaching Temperature

Tables 3 and 6 and Figures 8-10 show that at pulp densities of 2%, 3% and 4% solids, the amount of iron dissolved decreases quite markedly as the leaching temperature is increased. At the lowest pulp density there are no appreciable differences in the kinetics of magnesium oxide or the final magnesium concentration as the leaching temperature is increased from 3.5°C to 30°C. At a 3% solids pulp density, an increase in the leaching temperature from 15.5°C to 30°C does not alter the amount of magnesium oxide dissolved nor markedly affect the time to achieve complete reaction. The data shown in Figure 9 clearly indicate, however, that the kinetics of the dissolution reactions are markedly different; at 30°C massive precipitation of intermediate basic magnesium carbonate occurs and this is subsequently more rapidly converted to soluble magnesium bicarbonate than the dissolution of magnesium oxide at 15.5°C. At 4% solids, an insoluble basic magnesium carbonate is precipitated at leaching temperatures in the range 15.5-40°C. After about one hour this begins to react with the carbon dioxide forming soluble magnesium bicarbonate. At a leaching temperature of 15.5°C

all of the magnesium oxide is converted to the bicarbonate, but at the higher leaching temperatures the solubility limits of magnesium bicarbonate are exceeded such that at 30°C and 40°C only 70% and 30% respectively of the available magnesium is dissolved.

The data in Tables 3 and 6 and Figures 8-10 indicate that in the calcination/carbon dioxide pressure leach process, as high a leaching temperature should be used at as high a pulp density such that the solubility limit of magnesium bicarbonate is not exceeded.

Effect of Carbon Dioxide Pressure

It is apparent from Tables 3 and 7 and Figures 11 and 12 than an increase in carbon dioxide pressure results in a significant increase in the kinetics of magnesium oxide dissolution and a reduction of the time required for complete reaction. However, there is a substantial increase in the amount of iron dissolved. It is to be noted that at the pulp densities used, the amount of magnesium oxide dissolved is not affected by changes in the carbon dioxide pressure. At higher pulp densities it could be expected, on the basis of the solubility data discussed previously (1), that an increase in operating carbon dioxide pressure would result in an increase in the percentage magnesium dissolved.

From a process point of view, the carbon dioxide pressure should be kept as low as possible to ensure minimum iron dissolution but should be such that leaching times are not excessive. The lower operating pressure will also simplify the leaching equipment required.

Effect of Increased Agitation

Table 8 and Figure 13 show the effect of increased agitation on the kinetics of the magnesium oxide dissolution reaction at 3% solids, 15.5°C and 100 psig carbon dioxide. It is to be noted that kinetic curves for both magnesium oxide and iron oxide dissolution at the higher agitation rate are of the standard form expected for reaction between a solid and a gas dispersed throughout

the slurry. For magnesium oxide dissolution this indicates that any intermediate hydrated magnesium carbonate or basic magnesium carbonate formed is immediately converted to soluble magnesium bicarbonate. The increased agitation rate decreases the time for complete magnesium oxide dissolution but also results in significantly increased iron dissolution. It is not clear at this stage why the amount of iron dissolved should increase when the agitation rate is increased.

General Comments

For a given calcine the rate at which magnesium oxide dissolves and the amount of iron dissolved depend upon slaking time and temperature, pulp density, leaching temperature, carbon dioxide pressure and agitation. Except where the solubility limit of magnesium bicarbonate is exceeded, the above variables have no effect on the percentage of magnesium oxide that is dissolved. However, as Figure 14 shows, there is a pronounced general trend between the magnesium and iron contents of the pregnant liquors; as the magnesium concentration increases, so the iron concentration, in general, increases.

The amount of iron dissolution that can be tolerated is dependent on the grade of magnesium oxide required since, as noted above, the dissolved iron reports with the intermediate and final products. Thus the degree of iron dissolution will have an overriding effect on the determination of optimum leaching conditions.

If the amount of iron dissolution can be reduced or the soluble iron removed before the precipitation of the intermediate product from the clarified pregnant leach liquor, then it is clear that optimization of leaching variables will be less complex. In particular it will be possible to operate at the highest pulp density compatible with solubility limitations. It is the considered opinion of the authors that prevention of iron dissolution and/or the development of iron removal techniques are of the highest priority in the proposed programme for the next quarter.

ATMOSPHERIC PRESSURE LEACH - BULK CALCINE

As Table 9 and Figure 15 show, initially there is rapid reaction between magnesium oxide and carbon dioxide when the latter is bubbled at a rate of 5ℓ/min through a 3% solids slurry of the 700°C/3 h MAG 3 calcine. 71% of the magnesium is solubilized as magnesium bicarbonate after 0.5 h but then basic magnesium carbonate begins to precipitate and magnesium extraction falls to 55% after 1.25 h and remains constant even though leaching is extended for a significant time.

The data in Table 9 and Figure 15 are consistent with the data reported by Horiguchi (5) and also indicate that high pressure carbon dioxide is required for redissolution of the precipitated basic magnesium carbonate. Although atmospheric pressure leaching would require simpler leaching vessels and it would not be necessary to compress the carbon dioxide to any significant extent prior to leaching, the rapid precipitation of unreactive basic magnesium carbonate after maximum magnesium oxide dissolution is reached would make atmospheric pressure leaching less efficient and more difficult to control than pressure leaching.

PRESSURE LEACH TESTS - CALCINES FORMED UNDER DIFFERENT CONDITIONS

In the previous quarter, samples of the -¼"+7 mesh fraction of MAG 3 were subjected to calcination in a muffle furnace. Loss in weight on calcination and the X-ray diffraction patterns of the calcines were related to the temperature and time of calcination. The magnesium, calcium and iron contents of these calcines have now been determined and are given in Table 2. These calcines were crushed to 100% -100 mesh and leached at 3% solids, 0.5 h slake, 15.5°C, 100 psig carbon dioxide and 900 rpm. *These conditions do not necessarily represent optimum leaching conditions but do allow the effects of calcination conditions to be determined.* A different set of leaching conditions would probably yield different kinetic data but would not change, to any significant extent, the general trends with respect to calcination conditions noted below.

The leaching data as a function of calcination conditions are presented in Tables 10-13 and Figures 16-23. From Figure 22, which gives the magnesium extraction and [Fe × 100/Mg] concentration ratio for reactions that had gone to completion by the end of the 2.5 h leaching period, it can be seen that there is an optimum calcine magnesium content which in turn reflects the degree of calcination. Under calcination, giving a calcine with less than about 41% Mg, and over calcination, yielding calcines with greater than 41% Mg, both result in a reduction in magnesium extraction. It is also to be noted from Figures 22 and 23 that when reaction has gone to completion, the amount of iron dissolved follows a similar trend to that of magnesium. Moreover, there is a pronounced correlation between magnesium extraction and the [Fe × 100/Mg] concentration ratio of the pregnant liquor.

The data presented indicate that optimum calcination conditions for MAG 3 are of the order of 700°C for one hour. Calcination at 600°C for 3 hours, which gives a similar overall magnesium extraction, might be considered more favorable than 700°C/1 h. However, it is most likely that operating at a higher temperature for a shorter time would be preferable in energy and plant capacity terms.

For calcination temperatures in excess of 700°C, magnesium oxide leaching kinetics are significantly reduced, particularly as the calcination time is increased. As noted previously, these factors are related to the surface area of the calcines. At a calcination temperature of 700°C and calcination times shorter than one hour, insufficient magnesite is decomposed to magnesium oxide, while for a 5 hour calcination time, the kinetics of magnesium oxide dissolution are reduced such that after a leaching period of 2.5 h, the reaction is not complete.

It must be stressed that the above optimum calcination conditions refer to MAG 3. The chemical composition, weight loss on ignition, differential thermal and thermogravimetric curves and X-ray diffraction data for MAG 1 reported previously (1), as well as the chemical composition of the MAG 1 calcines reported here

(Table 1) clearly indicate that optimum calcination conditions for MAG 1 will be substantially different to those of MAG 3. It is thus apparent that optimum calcination conditions for a number of samples must be determined in order to assess optimum processing conditions.

RECOVERY OF INTERMEDIATE AND FINAL PRODUCTS

Theoretical Considerations

Magnesium bicarbonate, formed by carbonation of an aqueous slurry of magnesium oxide, is only stable in solution, its solubility being determined by temperature and carbon dioxide over pressure. If the temperature is increased or the carbon dioxide pressure reduced so that the solubility limits are exceeded, then a hydrated magnesium carbonate or a basic magnesium carbonate is precipitated.

In the calcination/carbon dioxide pressure leach process, the pregnant leach slurry is filtered to remove unreacted solids and excess carbon dioxide removed from the clarified pregnant liquor by air sparging or steam stripping. If the temperature of the pregnant liquor is above about $50^{o}C$ then a basic magnesium carbonate is precipitated; below this temperature a hydrated carbonate is formed (6). Nesquehonite, $MgCO_3 \cdot 3H_2O$, is the best known of the hydrated carbonates; other hydrates such as lansfordite, $MgCO_3 \cdot 5H_2O$, have been reported at solution temperatures below about $13^{o}C$. A number of basic magnesium carbonates have been reported in the literature (7), and of these, hydromagnesite is the best established. Even so, there is some confusion as to the composition of hydromagnesite; this has probably arisen because the formation of hydromagnesite appears to involve one or more intermediate phases (7). The generally accepted chemical formula of hydromagnesite is $Mg_5(CO_3)_4OH_2 \cdot 4H_2O$.

The precipitated hydrated carbonate or basic carbonate is calcined to form the final product of the process, magnesium oxide. The preferred intermediate precipitate is determined by

ease of precipitation

completeness of precipitation

ease of filtration
magnesium content
level of impurities
heat of calcination to MgO

The chemical and physical properties of the magnesium oxide such as bulk density, are mainly determined by the temperature of calcination of the intermediate precipitate. The nature of the intermediate precipitate also has a bearing on the properties of the magnesium oxide product.

Results

The clarified pregnant liquor from run number 10 containing 6.50 gpℓ magnesium and 0.015 gpℓ iron was divided into two equal amounts. One sample was heated to 65 ± 2°C and sparged with air at 1 ℓ/min; the other sample was kept at room temperature (20 ± 2°C) and also sparged with air at 1 ℓ/min. A white fluffy precipitate readily formed in the bulk of the high temperature solution; this precipitate settled quite quickly once agitation was stopped. Precipitation of a fine white crystalline solid took place in the room temperature solution. This crystalline precipitate formed on the walls of the vessel and could only be removed by mechanical scraping.

The two precipitates were recovered by vacuum filtration, washed with a minimum volume of cold water and air dried at 20 ± 2°C over several days. Chemical analysis gave the following data (%):

	MgO	CaO	Fe_2O_3	CO_2	H_2O*
Low Temperature Precipitate	28.85	0.126	0.031	35.13	35.86
High Temperature Precipitate	39.03	0.704	0.050	40.70	19.52

These data clearly indicate that although the low temperature precipitate has a lower MgO content, it has a significantly lower impurity level than the high temperature precipitate.

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*By difference.

X-ray diffraction data showed that the low temperature product was nesquehonite, $MgCO_3 \cdot 3H_2O$.* The differential thermal and thermogravimetric analysis curves of this phase are shown in Figure 24 and are similar to those reported by Davies and Bubela (7) for nesquehonite. The curves suggest that water is lost below about 340°C; above this temperature carbon dioxide is evolved. The recorded weight loss (69.3%) is in good agreement with the theoretical weight loss of 71.3%. Nesquehonite decomposes according to the equation

$$MgCO_3 \cdot 3H_2O \longrightarrow MgO + CO_2 + 3H_2O \qquad \text{(viii)}$$

The heat of decomposition *per mole MgO product* is 53.60, 51.97 and 50.84 kcal at 600, 800 and 1000°C respectively.

The X-ray diffraction pattern of the high temperature precipitate is quite complex; the major phase appears to be hydromagnesite (ASTM: 25-513) with small amounts of of protohydromagnesite (7) and dypingite (ASTM: 23-1219). The differential thermal and thermogravimetric analysis curves of this precipitate, shown in Figure 25, are similar to those of protohydromagnesite, a partially decarbonated and dehydrated intermediate between nesquehonite and hydromagnesite. The weight loss of 58.0% is quite close to that expected for protohydromagnesite (60.8%) but much lower than that for hydromagnesite (72.6%). However, the chemical analysis and composition calculated from the weight loss curve appear to be nearer to that of hydromagnesite than of protohydromagnesite.

	Chemical Analysis†	TGA Curve	Protohydro-magnesite	Hydro-magnesite
MgO (%)	39.03	42.03	32.20	38.58
CO_2 (%)	40.70	36.03	33.30	39.70
H_2O (%)	19.52 ‡	21.94	34.50	21.72

*The reference XRD data (ASTM: 20-669) have been shown (8) to be incorrect with respect to several reflection intensities.

†Contains 0.704% CaO and 0.050% Fe_2O_3.

‡By difference.

On the basis of the data available, it is considered that the high temperature precipitate is principally hydromagnesite. The latter undergoes thermal decomposition according to the equation

$$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O \longrightarrow 5MgO + 4CO_2 + 5H_2O \qquad (ix)$$

the heat of decomposition *per mole of MgO product* is 34.91, 35.62 and 36.58 kcal at 600, 800 and 1000°C respectively.

Samples of both precipitates were calcined in air at 900°C for 20 hours. Chemical analysis of the products yielded the following data (%)

	MgO	CaO	Fe_2O_3	Total
Low Temperature	97.0	0.511	0.106	97.6
High Temperature	96.2	1.78	0.120	98.1

It is known that magnesium oxide produced at calcination temperatures in excess of 750°C tends to absorb both carbon dioxide and water from the atmosphere. Both of the above calcines appeared hygroscopic and this probably accounts for analytical totals less than 100%.

At the present stage it is considered that the higher bulk density and purity of nesquehonite and the magnesium oxide derived therefrom make low temperature precipitation more favourable in process terms. This is despite the fact that high temperature precipitation yields a product which forms in the bulk of the solution and which requires less energy for decomposition to magnesium oxide. Rates of precipitation and degree of precipitation have not been determined as yet and these will have a bearing on optimum process conditions.

The remaining pregnant solutions were separately stored at ambient temperature (20 ± 2°C). In each case a crystalline solid formed on the surface of the mother liquor and on the walls of the vessel. Precipitation was quite slow and took place over several days. Solutions which initially had a high iron content and were red-brown in colour gave precipitates of a similar colour, indicating

coprecipitation of iron oxide. The mother liquors were colourless once precipitation had gone to completion. In all cases the major phase was in the form of acicular prismatic needles (Figure 26). Occasionally, however, larger prismatic crystals were also present (Figure 27). X-ray diffraction analysis confirmed that the acicular needles were nesquehonite, $MgCO_3 \cdot 3H_2O$. X-ray analysis of several handpicked prismatic crystals gave reflections that could not be accounted for by any known normal or basic carbonates of magnesium for which X-ray diffraction data are currently available. Single crystal studies, carried out by Dr. R. Hill of this Division, have shown that this phase is in fact lansfordite, $MgCO_3 \cdot 5H_2O$. According to the literature this phase is only stable below about 13°C, but the fact that it was formed from liquors at 20 ± 2°C indicates that it is metastable above 13°C. The upper level of stability of lansfordite has not as yet been determined although it has been observed as a solid in a solution held at 27°C for several days. From a process point of view, it is obvious that precipitation of lansfordite should be kept to a minimum since it has a lower magnesium content and requires more energy for decomposition than does nesquehonite.

PROCESS DESIGN - PRESENT VIEWS

The above results and discussion indicate that the calcination/carbon dioxide pressure leach process is more complex than originally considered. The results also indicate that more laboratory scale testwork should be carried out before technical scale testwork is commenced. The content of the future experimental programme (laboratory and technical scale) is based upon the data obtained to date and the simplified proposed flowsheet shown in Figure 28. The flowsheet assumes that only one product of a fixed specification is to be produced. We are led to believe that most magnesia operations produce more than one grade of product. It is important to note that the technical scale studies may indicate alterations to the proposed flowsheet.

On the basis of the results reported here and reference to standard chemical engineering textbooks, the following comments can

be made with respect to the proposed flowsheet. Mass, heat and volume balances have not been carried out as yet, although energy requirements have been determined for several specific unit operations. Complete data cannot be calculated since insufficient information on the orebody, product specification, etc., is currently available. What is clear, however, is that the plant will be quite large; the size is principally determined by the optimum pulp density. If the maximum pulp density, as determined by the level of iron dissolution, is 3% solids, which gives a pregnant liquor containing about 10 gpℓ magnesium, then 60 tonne of process water passes through the circuit for each tonne of magnesium oxide product.

ORE MINING AND STOCKPILING

Because the optimum calcination conditions vary with the magnesite/dolomite ratio of the feed, it will be essential that the orebody be carefully assayed before mining and that mining be carried out on a controlled pattern. If the dolomite content of the orebody is low and occurs as distinct lenses, pods or beds, then because of its lower magnesium carbonate content compared with that of magnesite, it would probably be advantageous to reject this ore. If, however, the orebody contains a substantial amount of dolomite such that it accounts for a considerable proportion of the recoverable magnesium oxide, then blending of the mineral ore will be necessary to give a reasonably uniform process feed. The degree of blending required can be partly achieved by selective mining and will be completed during crushing and grinding.

CRUSHING CIRCUIT

Mined ore needs to be crushed to a suitable size for efficient calcination. The crushed ore needs to be of a size which will permit even yet complete calcination. As noted below, calcination conditions need to be carefully controlled and it is considered that crushing to minus 1/2 inch would probably be adequate. Because of the hardness of the magnesite/dolomite ore, crushing would probably have to be carried out in several stages with recycling of oversize ore between each stage. This would ensure that there is not

excessive particle size reduction which would lead to inefficient calcination, and would also increase the efficiency of blending.

ORE CALCINATION

For efficient leaching and adequate recoveries, calcination must be carefully controlled. Optimum conditions (time and temperature) are fixed by particle size and feed composition. During calcination, carbon dioxide is evolved and this needs to be recovered from the flue gases for the subsequent leaching step.

The standard method for calcining magnesite/dolomite ores is in directly fired rotary kilns. Fuel oil, LPG or coal, together with the appropriate quantity of air, are used for firing purposes. The off-gases from such a kiln would have a relatively low carbon dioxide content, probably of the order of 30% by volume. The dilution of the off-gases by excess air, nitrogen and unburnt hydrocarbons would be advantageous as it has previously been shown (1) that removal of the carbon dioxide above the calcined ore increases the efficiency of calcination. Control of directly fired rotary kilns is not readily achieved and there is a significant possibility of a certain amount of ore being heated to excessive temperatures in the region of the burner flame.

Greater temperature control can be achieved in indirectly fired rotary kilns, but there are significantly greater engineering problems associated with their operation. In addition they are likely to have higher capital and operating costs than directly fired rotary kilns. The use of indirectly fired rotary kilns would be advantageous in that the off-gases would have a very high carbon dioxide content. This would reduce both the load on the compressors and the total pressure in the leaching vessels.

MILLING CIRCUIT

To achieve an acceptable leaching rate, it is normally necessary to reduce the feed size to 90% -100 mesh. Calcined magnesite is relatively soft and size reduction would be readily

achieved in a conventional milling circuit. Any quartz present in the calcined ore could be selectively screened out during size reduction. Milling is most easily carried out as a wet process where the ore is slurried to about 40-50% solids. The use of wet milling reduces dust problems and also allows the feed to be readily transferred to the leaching vessels. Dry milling, however, might be preferable since this would reduce iron dissolution during slaking.

As noted previously, calcined ore readily undergoes hydrolysis (slaking), the major reaction being

$$MgO + H_2O \longrightarrow Mg(OH)_2 \qquad \text{(ii)}$$

This reaction is highly exothermic, and as the data presented above clearly show, prolonged slaking at an elevated temperature leads to excessive iron dissolution during leaching. Thus it will be necessary to cool the calcine to ambient temperature before wet milling, which must be carried out as quickly as possible with removal of the heat generated by reaction (ii).

LEACHING CIRCUIT

On the basis of the data obtained to date, leaching of the calcined ore will be carried out at a relatively low carbon dioxide partial pressure ($\lesssim$ 100 psig). Together with the relatively non-corrosive nature of aqueous carbon dioxide, this indicates that leaching can be carried out in relatively simple mild steel leaching vessels. The slurry from the milling circuit requires dilution prior to injection of the carbon dioxide; the water required for this purpose is derived from other areas of the overall process. The operating pulp density is determined principally by the leach temperature and the amount of iron dissolution that can be tolerated.

Because leaching is highly exothermic and magnesium bicarbonate solubility decreases with increasing temperature, the leaching vessels must be efficiently cooled to an operating temperature of about 30°C. The carbon dioxide required for leaching is derived from several unit operations in the overall process; ore

calcination, off-gases from the first precipitation stage and product calcination. These off-gases must be compressed to a suitable pressure and preferably freed of non-reactive components such as nitrogen and oxygen; the higher the carbon dioxide content of the reaction mixture, the lower the total operating pressure.

It has yet to be established whether or not a continuous counter current leaching circuit would be the most appropriate; previous experience in these laboratories with a variety of non-ferrous metal leaching systems suggests that it probably would.

SOLID/LIQUID SEPARATION

After the desired retention time the pregnant liquor is separated from the leach residue. This separation must be carried out rapidly and preferably under a carbon dioxide atmosphere to prevent precipitation of hydrated magnesium carbonate. The laboratory scale tests showed that the solids in the pregnant leach slurries settle quite rapidly although filtration rates are relatively slow. These facts suggest that pressure filtration would probably be the most suitable solid/liquid separation technique.

IRON PRECIPITATION

An iron precipitation stage has been incorporated in case it is not practical to leach under conditions which yield a pregnant liquor with a very low iron content.

INTERMEDIATE PRODUCT PRECIPITATION

A two-stage precipitation circuit is proposed to permit a carbon dioxide-rich stream to be recovered for re-use in the leaching circuit. Initial precipitation is achieved by injection of steam; to precipitate nesquehonite, $MgCO_3 \cdot 3H_2O$, the temperature of the slurry would have to be kept below about $50^{\circ}C$. In the second stage most of the remaining soluble magnesium bicarbonate is precipitated by aeration.

INTERMEDIATE PRODUCT RECOVERY

The precipitated nesquehonite is recovered as a wet slurry by clarification and filtration. The filtrate is subjected to a purification step and returned to the milling/leaching circuits. The wet slurry is dried at $\leq 350^{\circ}C$ to remove excess water and water of crystallization leaving essentially anhydrous magnesium carbonate. Provided there is no stickiness problem, rotary kilns or fluidized bed driers would be suitable for this stage.

PRODUCT RECOVERY

Anhydrous magnesium carbonate is converted to the product, MgO, by calcination in a rotary kiln, the carbon dioxide in the off-gases recovered for use in the leaching circuit. The temperature of calcination is normally in the 1000-2000$^{\circ}C$ range, the actual temperature being determined by the required physical and chemical properties of the product.

SUMMARY OF RESULTS/GENERAL CONCLUSIONS

- Chemical analyses of calcines are consistent with their X-ray diffraction patterns and the corresponding weight loss on ignition and can be used to ascertain the temperature/time profile to which they have been subjected.

- Iron oxide is dissolved to a significantly greater extent than the literature indicates. Because the soluble iron reports with the intermediate and final products, the level of iron dissolution that can be tolerated is determined by market requirements.

- For a given calcine, magnesium and iron dissolution depend upon slaking time and temperature, pulp density, temperature, carbon dioxide partial pressure and agitation.

- Apart from temperature, the above leaching variables have virtually no effect on the percentage magnesium extracted although the kinetics of magnesium oxide dissolution may be altered.

- At the elevated temperatures and/or low carbon dioxide pressure there may be precipitation of a basic magnesium carbonate during the early stages of leaching. This precipitate dissolves quite rapidly as the leaching time is extended provided the solubility limit of magnesium bicarbonate is not exceeded and the carbon dioxide pressure is greater than atmospheric pressure.

- The amount of iron dissolved increases as slake time and temperature, pulp density, carbon dioxide pressure and agitation rate are increased and the leaching temperature decreased.

- Using a fixed set of leaching conditions, which do not necessarily represent optimum leaching conditions, it is readily shown that calcination temperature and to a lesser extent calcination time, has a pronounced effect on the percentage and rate of magnesium oxide dissolution.

- For MAG 3 calcines where magnesium oxide dissolution has gone to completion at the end of the specified leaching period, there is a direct correlation between the amount of magnesium and iron dissolved; the greater the magnesium dissolution the greater the iron dissolution. For the same series of calcines there is an optimum magnesium content with respect to amount of magnesium dissolved. This approximates to calcination at 700^{o}C for one hour. At a lower calcination temperature there is incomplete conversion of magnesium carbonate to magnesium oxide, while at higher calcination temperatures there is a reduction in reactivity due to a decrease in surface area.

- Optimum calcination conditions depend upon the magnesite/dolomite content ratio of the feed.

- Two major products can be obtained from clarified pregnant leach liquors. These have different physical and chemical properties although both yield the desired product, magnesium oxide, at approximately the same calcination temperature. Low temperature precipitation yields nesquehonite, $MgCO_3 \cdot 3H_2O$. This has a higher bulk density and purity than the high temperature precipitate hydromagnesite, $Mg_5(CO_5)_4(OH)_2 \cdot 4H_2O$, whereas the latter

has a lower heat of decomposition per mole of MgO product and is easier to recover from the precipitation vessel.

- A relatively simple proposed flowsheet for the calcination/carbon dioxide pressure leach process is described in detail, but because of the current lack of information regarding ore composition (particularly the magnesite/dolomite ratio), product quantity and quality, etc., detailed mass, heat and volume balances cannot be carried out.

PROPOSED FUTURE WORK PROGRAMME

It is clear from the above results and discussion that a considerable amount of laboratory scale experimental work should be carried out before technical scale calcination and leaching studies are planned and executed. It is also considered that reasonably detailed process design and costing should be carried out before the technical scale tests are commenced.

During the next three months period, it is proposed that the following be carried out:

- Further leaching tests investigating the influence of agitation rate and leach liquor composition on magnesium and iron extraction rates, and the development of leaching conditions which reduce iron dissolution.

- Development of methods for removing dissolved iron from pregnant leach slurries prior to precipitation of intermediate products.

- Determination of optimum calcination conditions for sample MAG 1 using standard leaching conditions.

- Determination of rates and degrees of precipitation of intermediate products.

- Preparation of a range of final products and determination of their physical and chemical properties.

- Detailed process design and costing studies.

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TABLE 1

Chemical Analyses (%) of MAG 1 Calcines[a]

Calcination Conditions		Mg	Ca	Fe
Temperature (°C)	Time (h)			
600	1	13.6	18.2	1.25
700	1	15.1	21.2	1.35
800	1	17.6	23.3	1.49
850	1	17.6	24.8	1.49
970	1	21.9	29.1	1.86
590	3	13.8	18.7	1.21
700	3	16.6	20.0	1.43
850	3	21.2	28.8	1.84
970	3	22.6	30.8	1.88
700	0.25	13.2	17.6	1.16
700	0.5	14.4	19.3	1.24
700	1	15.1	21.2	1.35
700	2	16.7	22.8	1.39
700	3	16.6	20.0	1.43
700	5	16.5	21.9	1.41
850	0.25	16.1	21.2	1.28
850	0.5	17.4	23.4	1.55
850	1	17.6	24.8	1.49
850	2	20.6	28.3	1.74
850	3	21.2	28.8	1.84

a The sample initially contains (%) Mg 12.8, Ca 17.7 and Fe 0.915.

TABLE 2

Chemical Analyses (%) of MAG 3 Calcines[a]

Calcination Conditions		Mg	Ca	Fe
Temperature (°C)	Time (h)			
600	1	29.4	3.84	2.13
700	1	40.8	5.65	2.97
800	1	44.6	5.42	3.19
850	1	46.5	5.81	3.31
970	1	46.3	5.81	3.26
590	3	41.0	4.95	2.93
700	3	43.0	5.51	3.07
850	3	45.8	5.86	3.26
970	3	45.1	6.25	3.25
700	0.25	26.2	3.57	1.85
700	0.5	33.5	4.27	2.42
700	1	40.8	5.65	2.97
700	2	43.5	5.67	3.03
700	3	43.0	5.51	3.07
700	5	43.3	5.43	3.09
850	0.25	34.7	5.16	2.45
850	0.5	44.2	5.76	3.15
850	1	46.5	5.81	3.31
850	2	46.1	6.12	3.27
850	3	45.8	5.86	3.26

a The sample initially contains (%) Mg 23.6, Ca 3.34 and Fe 1.84.

TABLE 3

Autoclave Leach Test Data - Effect of Leaching Conditions

Sample: MAG 3
Particle Size: -¼"+7 mesh ground to 100% -100 mesh
Calcination Conditions: 700°C for 3 h
Leach Conditions: 1 litre water (Mg and Fe free), 900 rpm

Run Number	8	9	10		11[b]		12[b]		13	
Calcine Weight (g)	20	20	20		20		20		20	
Slake Time (h)	0.5	0.5	0.5		0.5		16.75		0.5	
Slake Temperature (°C)	15.5	15.5	15.5		15.5		15.5		15.5	
Leach Temperature (°C)	15.5	15.5	15.5		15.5		15.5		15.5	
CO_2 Pressure (psig)	100	100	100		25		25		50	
Leach Time (h)	Pregnant Liquor Composition (gpℓ)									
	Mg	Mg	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe
0.08	1.00	1.30	1.20	0	0.40	0	0.20	0	0.60	0
0.25	1.60	1.66	1.40	0	0.90	0	0.40	0	1.60	0
0.50	2.70	2.50	2.96	0	1.30	0	1.06	0	2.00	0
0.75	4.40	4.24	4.08	0.010	1.50	0	1.68	0	2.60	0
1.00	5.60	5.45	5.80	0.015	1.60	0	2.50	0	2.80	0
1.25	6.50	6.32	6.20	0.015	1.70	0	3.35	0.001	3.10	0
1.50	6.60	6.42	6.30	0.015	1.80	0	4.10	0.005	4.50	0.002
1.75	6.60	6.42	6.50	0.015	1.86	0	5.00	0.010	6.40	0.005
2.00	6.60	6.42	6.50	0.015	3.20	0.001	5.80	0.020	6.54	0.006
2.25					4.55	0.002	6.50	0.030	6.60	0.006
2.50					6.10	0.004	6.60	0.036	6.60	0.006
2.75					6.70	0.005	6.60	0.040		
3.00					6.75	0.005	6.60	0.040		
3.25					6.70	0.005	6.65	0.040		
(Fe × 100/Mg) of Final Liquor			0.23		0.07		0.60		0.09	
Mg Extraction (%)	84	82	83		86		85		84	

a Based on calcine composition of 39.1% Mg.

b Precipitation of basic carbonate apparent in early stages of leach test.

Table 3 (continued)

Autoclave Leach Test Data - Effect of Leaching Conditions

Sample: MAG 3
Particle Size: -¼"+7 mesh ground to 100% -100 mesh
Calcination Conditions: 700°C for 3 h
Leach Conditions: 1 litre water (Mg and Fe free), 900 rpm

095

Run Number	14		15		16		17		18[b] [c]		19	
Calcine weight (g)	20		20		30		40		50		20	
Slake Time (h)	0.5		0.5		0.5		0.5		0.5		0.5	
Slake Temperature (°C)	3.5		3.5		15.5		15.5		15.5		30.0	
Leach Temperature (°C)	3.5		3.5		15.5		15.5		15.5		30.0	
CO_2 Pressure (psig)	100		25		100		100		100		100	
Leach Time (h)	Pregnant Liquor Composition (gpℓ)											
	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe
0.08	1.10	0	1.00	0	0.60	0	0.40	0	1.56	0	0.80	0
0.25	1.54	0	1.10	0	1.70	0	1.40	0	2.20	0	1.76	0
0.50	2.70	0	1.40	0	3.16	0	2.10	0	2.20	0	2.20	0
0.75	4.60	0.003	2.00	0	3.68	0.001	1.94	0	1.40	0.002	4.90	0
1.00	6.00	0.008	2.75	0.001	4.18	0.001	1.40	0	1.16	0.005	6.30	0
1.25	6.30	0.012	3.40	0.003	6.60	0.020	1.64	0	1.46	0.008	6.50	0
1.50	6.50	0.016	4.35	0.005	9.28	0.042	4.30	0.002	3.36	0.010	6.60	0
1.75	6.46	0.018	5.00	0.006	9.44	0.054	7.30	0.015	8.00	0.020	6.60	0
2.00	6.50	0.020	5.90	0.008	9.50	0.054	10.78	0.072	12.60	0.050	6.60	0
2.25	6.46	0.021	6.30	0.011	9.50	0.054	13.00	0.095	16.54	0.124		
2.50			6.35	0.012	9.50	0.054	13.10	0.100	16.50	0.148		
2.75			6.35	0.013			13.10	0.104	16.50	0.156		
3.00							13.05	0.140	16.54	0.176		
3.25									16.54	0.180		
3.50									16.54	0.180		
(Fe × 100/Mg) of Final Liquor	0.33		0.20		0.58		0.80		1.09		0	
Mg Extraction (%)[a]	83		81		81		84		85		84	

[a] Based on calcine composition of 39.1% Mg.
[b] Precipitation of basic carbonate apparent in early stages of leach test.
[c] After 4.0, 4.5 and 5.0 h, carbon dioxide pressure reduced to 50 psig, 25 psig and 0, respectively. Magnesium content of liquor 0.5 h after each pressure reduction was 16.40, 15.30 and 14.00 gpℓ, respectively. Precipitation of basic carbonate apparent when final measurement made.

TABLE 3 (continued)

Autoclave Leach Test Data - Effect of Leaching Conditions

Sample: MAG 3
Particle Size: -¼"+7 mesh ground to 100% -100 mesh
Calcination Conditions: 700°C for 3 h
Leach Conditions: 1 litre water (Mg and Fe free), 900 rpm

Run Number	20		21[b c]		22[d]		23		24[b]		25	
Calcine Weight (g)	40		40		30		30		30		30	
Slake Time (h)	0.5		0.5		0.5		17.25		0.5		0.1	
Slake Temperature (°C)	30.0		40.0		85.0		15.5		30.0		15.5	
Leach Temperature (°C)	30.0		40.0		15.5		15.5		30.0		15.5	
CO_2 Pressure (psig)	100		100		100		100		100		100	
Leach Time (h)	Pregnant Liquor Composition (gpℓ)											
	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe
0.08	0.50	0	0.36	0	0.50	0	0.86	0	0.60	0	0.50	0
0.25	1.30	0	0.84	0	2.50	0.002	1.46	0	1.52	0	1.14	0
0.50	1.30	0	0.70	0	5.50	0.036	2.80	0.004	0.60	0	2.50	0.002
0.75	1.30	0	0.70	0	7.50	0.118	4.00	0.011	1.92	0	3.70	0.009
1.00	1.30	0.001	1.20	0	8.50	0.228	4.54	0.020	5.18	0.003	4.20	0.010
1.25	5.00	0.005	1.44	0	9.10	0.284	7.86	0.066	9.30	0.010	6.00	0.017
1.50	8.40	0.015	2.50	0	9.50	0.306	9.50	0.162	9.30	0.012	9.20	0.045
1.75	9.90	0.020	4.00	0.004	9.50	0.320	9.50	0.180	9.30	0.012	10.00	0.053
2.00	11.00	0.020	6.00	0.006	9.50	0.328	9.70	0.182	9.34	0.011	10.30	0.055
2.25	11.10	0.020	6.02	0.006	9.50	0.332	9.70	0.182	9.32	0.011	10.30	0.055
2.50	11.00	0.020	6.00	0.006	9.50	0.332	9.70	0.182	9.30	0.012	10.30	0.055
2.75			6.00	0.006								
(Fe × 100/Mg of Final Liquor	0.18		0.10		3.49		1.88		0.13		0.53	
Mg Extraction[a]	70		30		81		83		79		88	

a Based on calcine composition of 39.1% Mg.
b Precipitation of basic carbonate apparent during all stages of leach test.
c After 2.75 h temperature dropped to 15.5°C over 0.75 h; at this time the pregnant liquor contained 11.00 gpℓ Mg.
d Additional 0.3 h slake time required for cooling down from 85°C to 15.5°C.

TABLE 4

Magnesium Extraction (%) and (Fe × 100/Mg) Concentration Ratio as a Function of Slake Time and Temperature

Run Number	Slake Time (h)	Slake Temperature (°C)	Calcine Weight (g/ℓ)	Leach Temperature (°C)	CO_2 Pressure (psig)	Mg Extraction (%)	(Fe × 100/Mg)
11	0.5	15.5	20	15.5	25	86	0.07
12	16.75	15.5	20	15.5	25	85	0.60
25	0.1	15.5	30	15.5	100	88	0.53
16	0.5	15.5	30	15.5	100	81	0.58
23	17.25	15.5	30	15.5	100	83	1.88
16	0.5	15.5	30	15.5	100	81	0.58
22	0.5	85	30	15.5	100	81	3.49

TABLE 5

Magnesium Extraction (%) and (Fe × 100/Mg) Concentration Ratio as a Function of Pulp Density[a]

Run Number	Calcine Weight (g/ℓ)	Leach Temperature (°C)	Mg Extraction (%)	(Fe × 100/Mg)
10	20	15.5	83	0.23
16	30	15.5	81	0.58
17	40	15.5	84	0.80
18	50	15.5	85	1.09
19	20	30	84	0
24	30	30	79	0.13
20	40	30	70	0.18

a Slake time, slake temperature and CO_2 pressure are 0.5 h, leach temperature and 100 psig respectively.

TABLE 6

Magnesium Extraction (%) and (Fe × 100/Mg) Concentration Ratio as a Function of Leaching Temperature[a]

Run Number	Leach Temperature (°C)	Calcine Weight (g/ℓ)	Mg Extraction (%)	(Fe × 100/Mg)
14	3.5	20	83	0.33
10	15.5	20	83	0.23
19	30	20	84	0
16	15.5	30	81	0.58
24	30	30	79	0.13
17	15.5	40	84	0.80
20	30	40	70	0.18
21	40	40	30	0.10

a Slake time, slake temperature and CO_2 pressure are 0.5 h, leach temperature and 100 psig respectively.

TABLE 7

Magnesium Extraction (%) and (Fe × 100/Mg) Concentration Ratio as a Function of Carbon Dioxide Pressure

Run Number	CO_2 Pressure (psig)	Leach Temperature (°C)	Mg Extraction (%)	(Fe × 100/Mg)
15	25	3.5	81	0.20
14	100	3.5	83	0.33
11	25	15.5	86	0.07
13	50	15.5	84	0.09
10	100	15.5	83	0.23

TABLE 8

Autoclave Leach Test Data - Effect of Agitation

Sample: MAG 3
Particle Size: -¼"+7 mesh ground to 100% -100 mesh
Calcination Conditions: 700°C for 3 h
Leach Conditions: 30 g calcine/litre, 0.5 h, 15.5°C, 100 psig CO_2

Run Number	16		42	
Impeller Rotation (rpm)	900		1200	
Leach Time (h)	Pregnant Liquor Composition (gpℓ)			
	Mg	Fe	Mg	Fe
0.08	0.60	0	3.66	0.010
0.25	1.70	0	7.66	0.058
0.50	3.16	0	8.88	0.082
0.75	3.68	0.001	9.24	0.089
1.00	4.18	0.001	9.60	0.095
1.25	6.60	0.020	9.60	0.095
1.50	9.28	0.042	9.50	0.093
1.75	9.44	0.054	9.60	0.093
2.00	9.50	0.054	9.50	0.093
2.25	9.50	0.055		
2.50	9.50	0.055		
(Fe × 100/Mg) of Final Liquor	0.58		0.98	
Mg Extraction (%)[a]	81		81	

a Based on calcine composition of 39.1%.

TABLE 9

Atmospheric Pressure Leach Test Data

Sample:	MAG 3
Particle Size:	-¼"+7 mesh ground to 100% -100 mesh
Calcination Conditions:	700°C for 3 h
Leach Conditions:	30 g calcine/litre, 0.5 h slake (slurry temperature increased from 20 to 22°C), CO_2 flowrate 5 ℓ/min

Run Number	43[b]	
Leach Time (h)	Temperature (°C)	Pregnant Liquor Composition (gpℓ)
		Mg / Fe
0.08	26	1.91 / 0.001
0.25	30	5.71 / 0.025
0.50	31	8.30 / 0.036
0.75	29	7.62 / 0.025
1.00	26	6.73 / 0.011
1.25	24	6.48 / 0.009
1.50	22	6.53 / 0.008
1.75	20	6.50 / 0.007
2.00	20	6.50 / 0.008
2.25	20	6.50 / 0.007
2.50	20	6.50 / 0.007
16.50	20	6.45 / 0.006
(Fe × 100/Mg) of Final Liquor		0.11
Mg Extraction (%)[a]		55

a Based on calcine composition of 39.1% Mg.

b Precipitation of basic magnesium carbonate apparent after 0.75 h.

TABLE 10

Autoclave Leach Test Data - Effect of Calcination Conditions

Sample: MAG 3
Particle Size: -¼"+7 mesh ground to 100% -100 mesh
Leach Conditions: 30 g calcine/litre, 0.5 h slake, 15.5°C, 100 psig CO_2, 900 rpm

Run Number	26		27		28		29		30	
Calcination Temperature (°C)	600		700		800		850		970	
Calcination Time (h)	1		1		1		1		1	
Calcine Mg Content (%)	29.4		40.8		44.6		46.5		46.3	
Leach Time (h)	Pregnant Liquor Composition (gpℓ)									
	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe
0.08	0.70	0	0.20	0	0.20	0	0.76	0	0.60	0
0.25	1.20	0	0.64	0	0.56	0	0.80	0	0.72	0
0.50	2.43	0	2.10	0	1.60	0	0.90	0	1.30	0
0.75	3.22	0.001	3.70	0.002	2.80	0	1.64	0	1.55	0
1.00	3.60	0.001	4.20	0.004	6.00	0.003	2.25	0	1.66	0
1.25	3.71	0.001	6.20	0.043	7.20	0.006	2.66	0	1.84	0
1.50	3.86	0.001	8.40	0.050	7.74	0.008	3.20	0	2.16	0
1.75	3.85	0.001	10.40	0.056	8.00	0.012	3.64	0	2.38	0
2.00	3.85	0.001	11.05	0.064	8.40	0.014	4.00	0	2.66	0
2.25	3.86	0.001	11.05	0.066	8.80	0.016	4.40	0	3.00	0
2.50	3.85	0.001	11.05	0.063	9.15	0.017	4.90	0	3.46	0
(Fe × 100/Mg) of Final Liquor	0.03		0.57		0.19		0		0	
Mg Extraction (%)	44		90		68		35		25	

TABLE 11

Autoclave Leach Test Data - Effect of Calcination Conditions

Sample: MAG 3
Particle Size: -¼"+7 mesh ground to 100% -100 mesh
Leach Conditions: 30 g calcine/litre, 0.5 h slake, 15.5°C, 100 psig CO_2, 900 rpm

Run Number	31		32		33		34	
Calcination Temperature (°C)	590		700		850		970	
Calcination Time (h)	3		3		3		3	
Calcine Mg Content (%)	41.0		43.0		45.8		45.1	
Leach Time (h)	Pregnant Liquor Composition (gpℓ)							
	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe
0.08	0.86	0	0.54	0	0.05	0	0.14	0
0.25	1.60	0	1.50	0	0.18	0	0.24	0
0.50	2.50	0.002	3.10	0	0.56	0	0.58	0
0.75	3.10	0.004	4.20	0.002	0.88	0	0.95	0
1.00	3.74	0.006	5.40	0.009	1.18	0	1.32	0
1.25	4.90	0.012	7.14	0.016	1.56	0	1.50	0
1.50	7.96	0.031	8.60	0.026	1.78	0	1.64	0
1.75	9.70	0.052	10.00	0.034	2.22	0	1.76	0
2.00	10.34	0.054	10.40	0.039	2.80	0	1.86	0
2.25	10.34	0.054	10.54	0.041	3.50	0	2.12	0
2.50	10.34	0.054	10.54	0.042	3.94	0	2.50	0
(Fe × 100/Mg) of Final Liquor	0.51		0.40		0		0	
Mg Extraction (%)	84		82		29		18	

TABLE 12

Autoclave Leach Test Data - Effect of Calcination Conditions

Sample: MAG 3
Particle Size: -¼"+7 mesh ground to 100% -100 mesh
Leach Conditions: 30 g calcine/litre, 0.5 h slake, 15.5°C, 100 psig CO_2, 900 rpm

Run Number	35		36		27		37		32		38	
Calcination Temperature (°C)	700		700		700		700		700		700	
Calcination Time (h)	0.25		0.50		1		2		3		5	
Calcine Mg Content (%)	26.2		33.5		40.8		43.5		43.0		43.3	
Leach Time (h)	Pregnant Liquor Composition (gpℓ)											
	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe
0.08	0.48	0	0.70	0	0.20	0	0.40	0	0.54	0	0.20	0
0.25	1.06	0	1.44	0	0.64	0	1.20	0	1.50	0	0.80	0
0.50	1.34	0	2.78	0.004	2.10	0	2.50	0	3.10	0	2.10	0
0.75	1.38	0	4.36	0.015	3.70	0.002	3.90	0.002	4.20	0.002	3.60	0.004
1.00	1.40	0	5.56	0.016	4.20	0.004	5.60	0.012	5.54	0.009	5.20	0.013
1.25	1.54	0	5.84	0.017	6.20	0.043	7.70	0.020	7.14	0.016	6.80	0.022
1.50	1.54	0	5.84	0.016	8.40	0.050	9.40	0.034	8.60	0.026	8.50	0.042
1.75	1.54	0	5.84	0.015	10.40	0.056	10.30	0.048	10.00	0.034	9.30	0.050
2.00	1.48	0	5.84	0.015	11.05	0.064	10.70	0.054	10.40	0.039	10.00	0.053
2.25	1.48	0	5.88	0.015	11.05	0.066	10.80	0.056	10.54	0.041	10.30	0.058
2.50	1.54	0	5.88	0.015	11.05	0.063	10.90	0.056	10.54	0.042	10.60	0.061
(Fe × 100/Mg) of Final Liquor	0		0.26		0.57		0.51		0.40		0.58	
Mg Extraction (%)	20		59		90		84		82		82	

TABLE 13

Autoclave Leach Test Data - Effect of Calcination Conditions

Sample: MAG 3
Particle Size: -¼"+7 mesh ground to 100% -100 mesh
Leach Conditions: 30 g calcine/litre, 0.5 h slake, 15.5°C, 100 psig CO_2, 900 rpm

Run Number	39		40		29		41		33	
Calcination Temperature (°C)	850		850		850		850		850	
Calcination Time (h)	0.25		0.50		1		2		3	
Calcine Mg Content (%)	34.7		44.2		46.5		46.1		45.8	
Leach Time (h)	Pregnant Liquor Composition (gpℓ)									
	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe	Mg	Fe
0.08	0.30	0	0	0	0.76	0	0	0	0.05	0
0.25	1.30	0	0.40	0	0.80	0	0.08	0	0.18	0
0.50	2.60	0.002	1.46	0	0.90	0	0.47	0	0.56	0
0.75	4.00	0.012	2.70	0	1.64	0	0.91	0	0.88	0
1.00	5.30	0.017	3.88	0.002	2.25	0	1.60	0	1.18	0
1.25	5.70	0.020	4.94	0.003	2.66	0	2.21	0	1.56	0
1.50	6.10	0.022	5.62	0.004	3.20	0	2.90	0	1.78	0
1.75	6.40	0.022	6.20	0.006	3.64	0	3.45	0	2.22	0
2.00	6.40	0.022	6.70	0.007	4.00	0	4.19	0	2.80	0
2.25	6.40	0.022	7.29	0.009	4.40	0	4.55	0	3.50	0
2.50	6.40	0.022	7.74	0.009	4.90	0	5.10	0	3.94	0
(Fe × 100/Mg) of Final Liquor	0.34		0.12		0		0		0	
Mg Extraction (%)	62		58		35		37		29	

FIGURE 1. Technical scale rotary kiln. a - compressed air for purging; b - flowmeter; c - temperature controller; d - variable speed screw feeder; e - ore hopper; f - variable speed drive; g - calcine collection bin; h - outlet for off-gases.

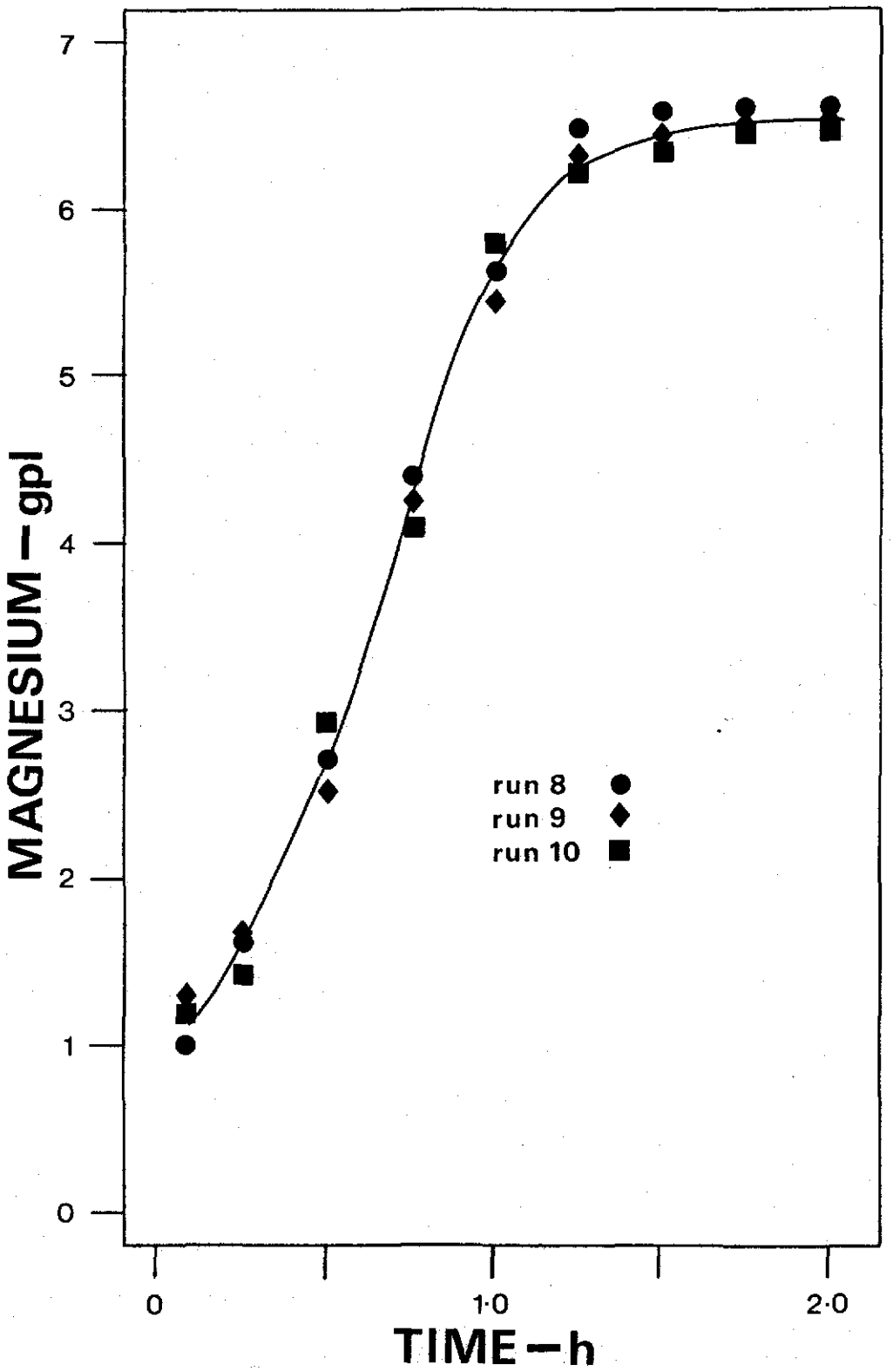

FIGURE 2. Autoclave leaching kinetic data; reproducibility. MAG 3 calcined at 700°C for 3 h, leached at 20 g solid/litre, 0.5 h slake, 15.5°C, 100 psig CO_2, 900 rpm. (See Table 3).

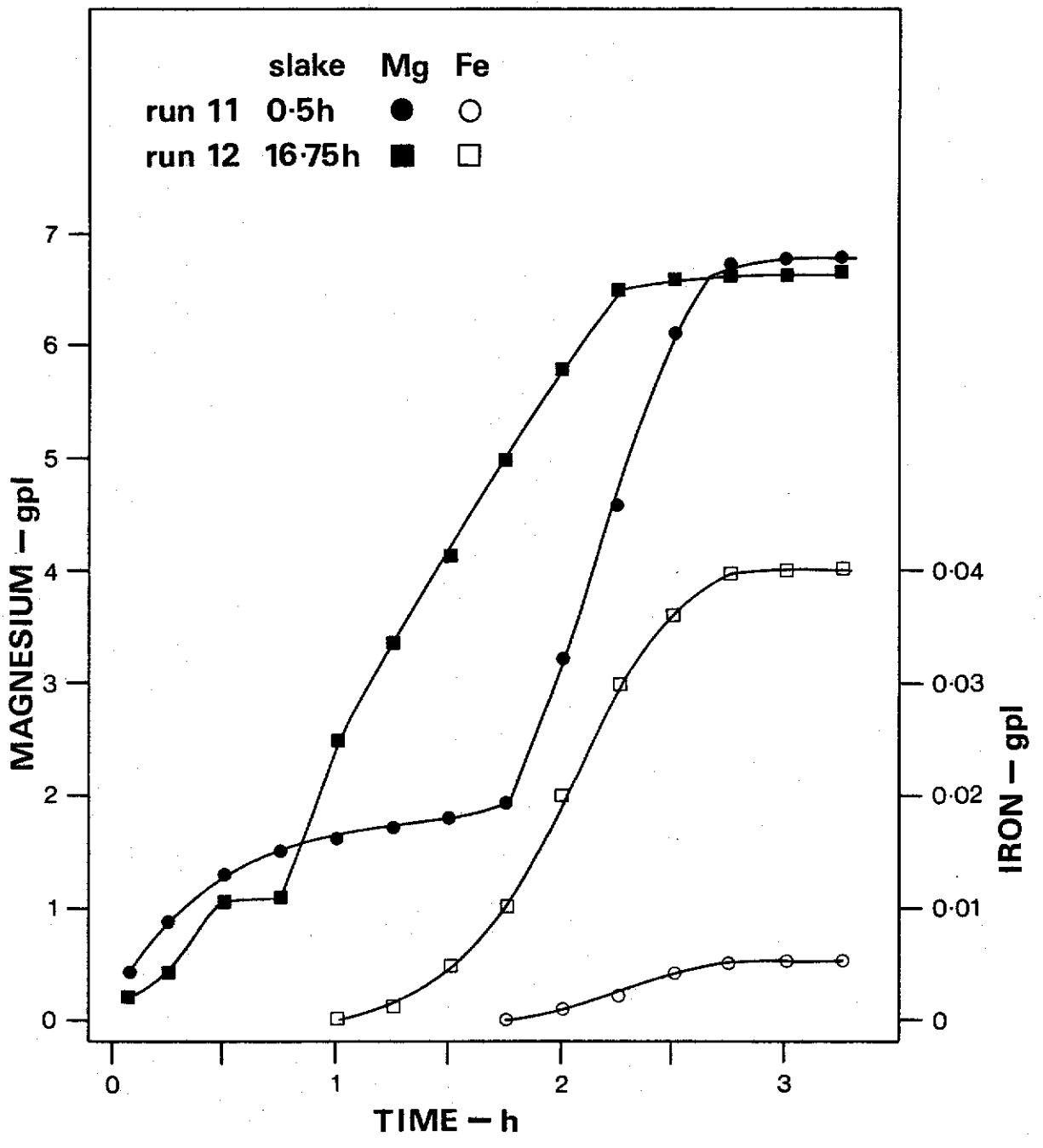

FIGURE 3. Autoclave leaching kinetic data; the effect of slaking period on magnesium and iron concentration. MAG 3 calcined at 700°C for 3 h, leached at 20 g solid/litre, 15.5°C, 25 psig CO_2, 900 rpm. (See Table 3).

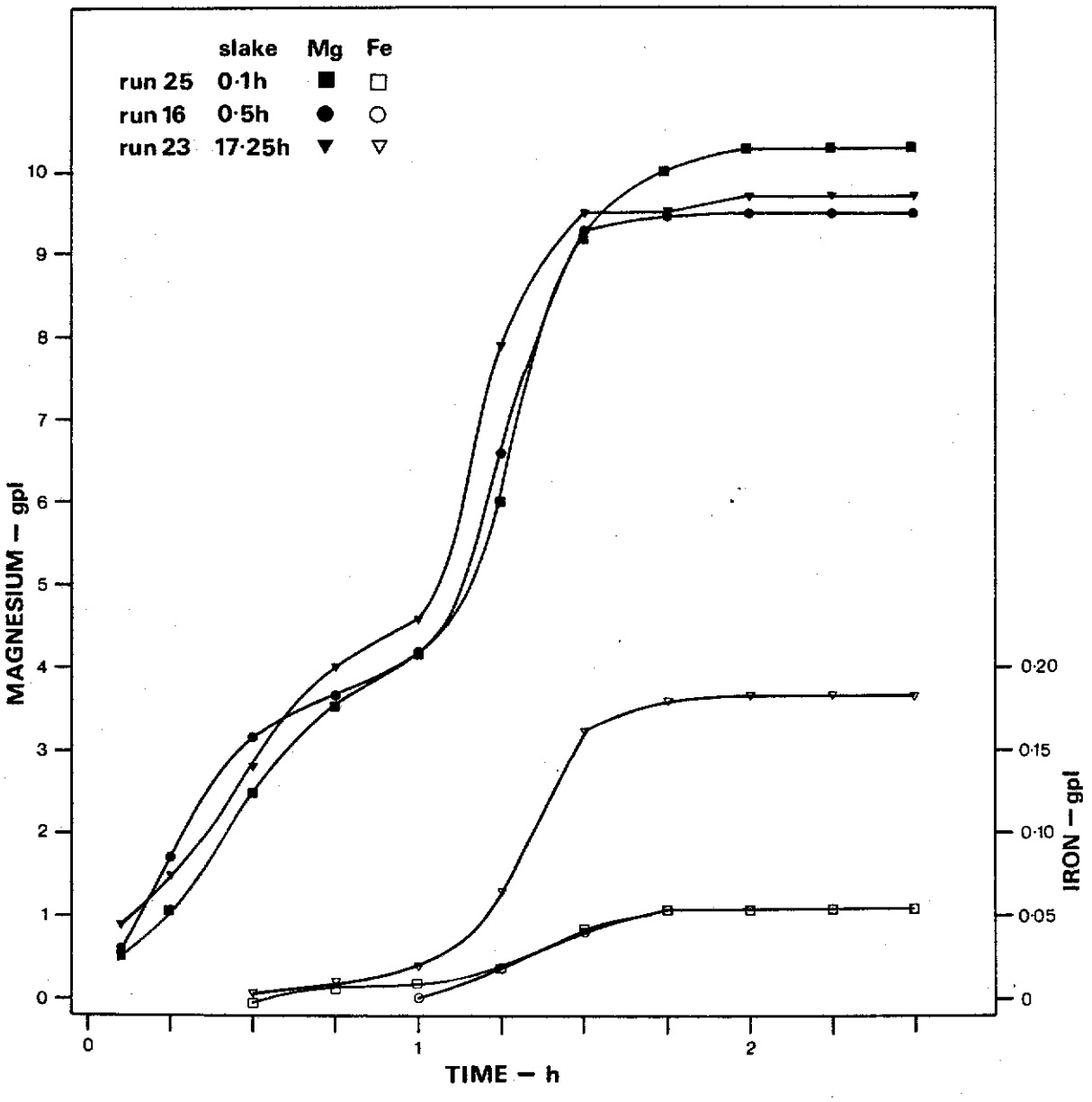

FIGURE 4. Autoclave leaching kinetic data; the effect of slaking period on magnesium and iron concentration. MAG 3 calcined at 700°C for 3 h, leached at 30 g solid/litre, 15.5°C, 100 psig CO_2, 900 rpm. (See Table 3).

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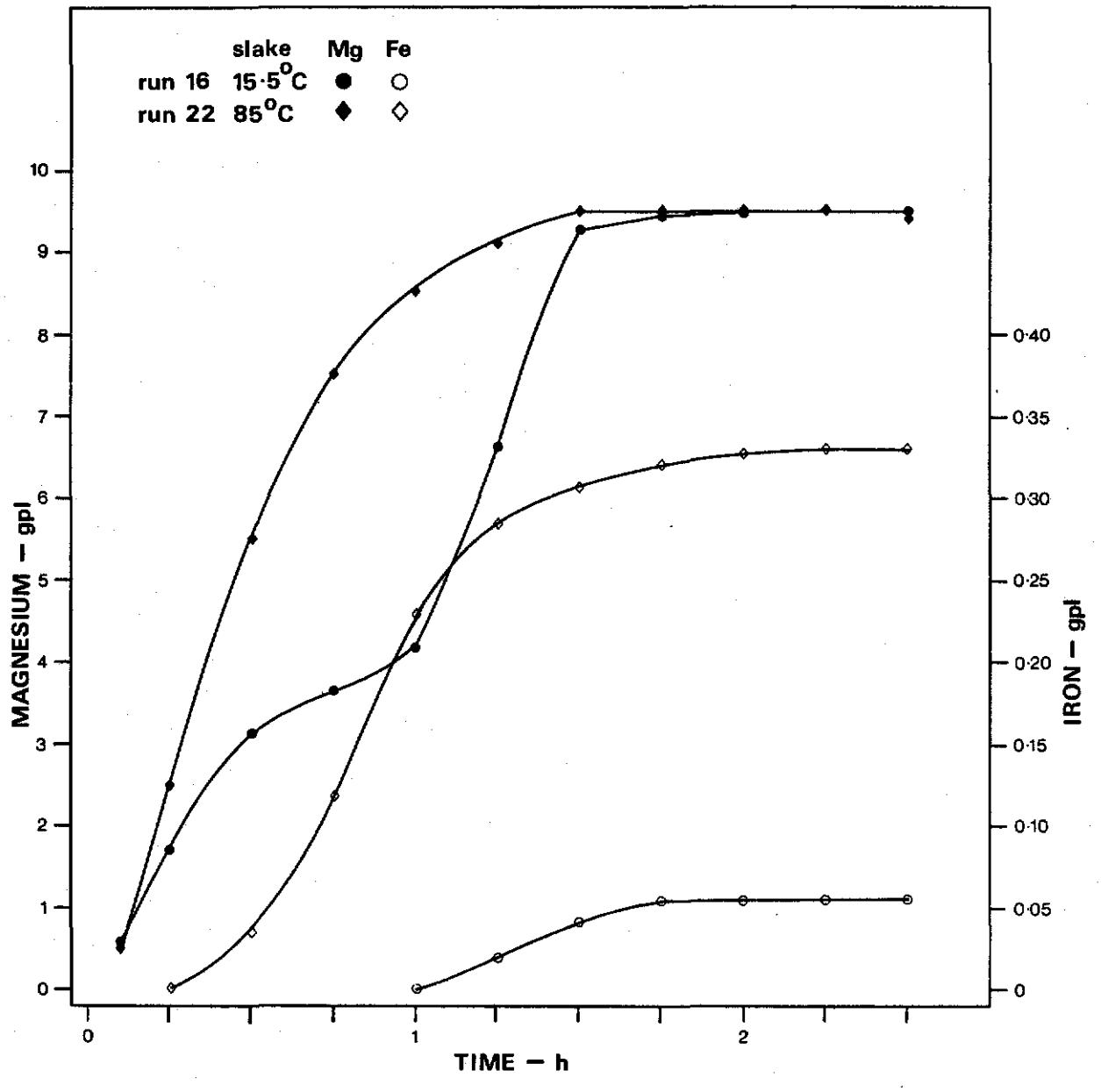

FIGURE 5. Autoclave leaching kinetic data; effect of slaking temperature on magnesium and iron concentration. MAG 3 calcined at 700°C for 3 h, leached at 30 g solid/litre, 0.5 h slake, 15.5°C, 100 psig CO_2, 900 rpm. (See Table 3).

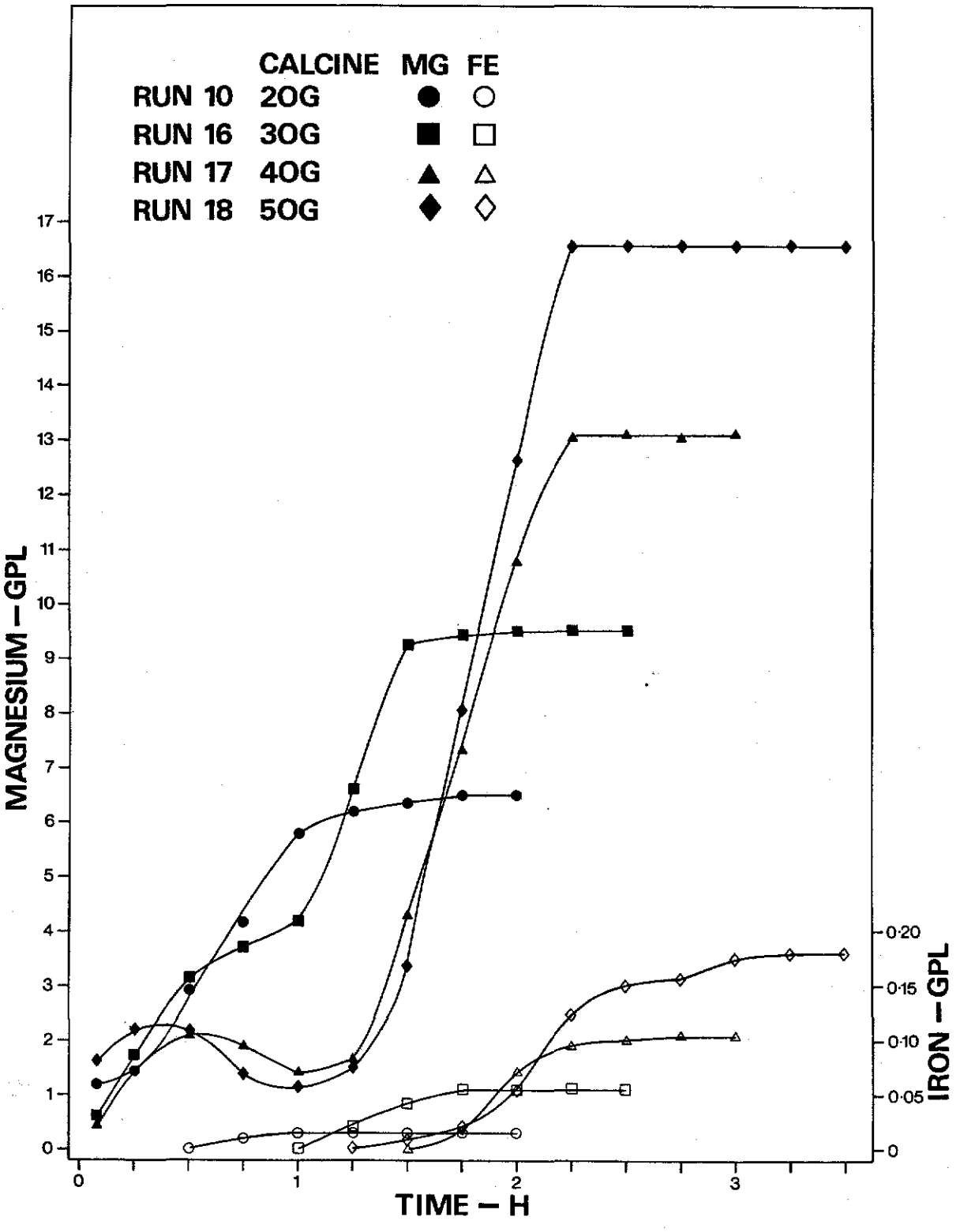

FIGURE 6. Autoclave leaching kinetic data; the effect of pulp density (g calcine/litre) on magnesium and iron concentration. MAG 3 calcined at 700°C for 3 h, leached at 15.5°C, 0.5 h slake, 100 psig CO_2, 900 rpm. (See Table 3).

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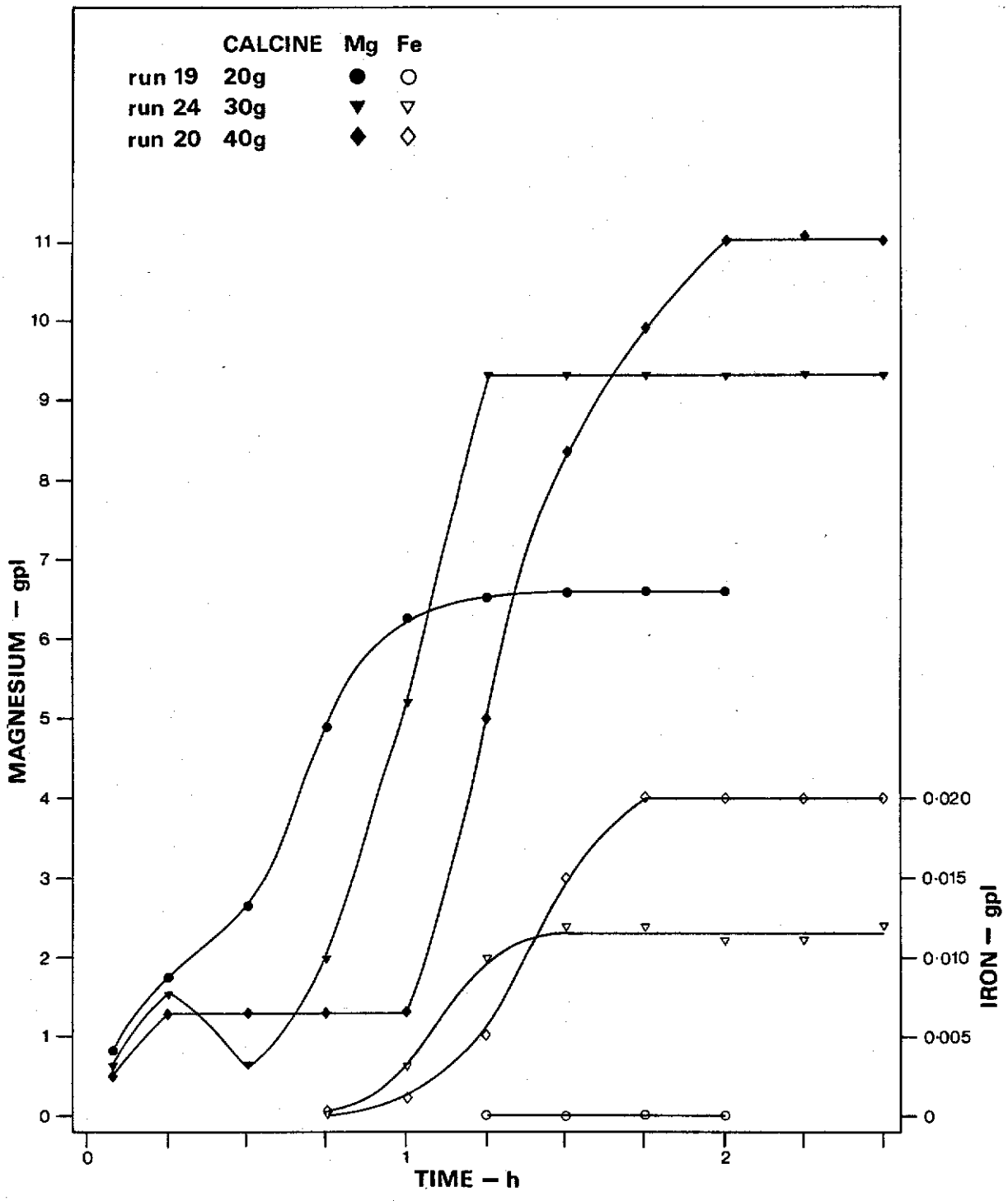

FIGURE 7. Autoclave leaching kinetic data; the effect of pulp density (g calcine/litre) on magnesium and iron concentration. MAG 3 calcined at 700°C for 3 h, leached at 30°C, 0.5 h slake, 100 psig CO_2, 900 rpm. (See Table 3).

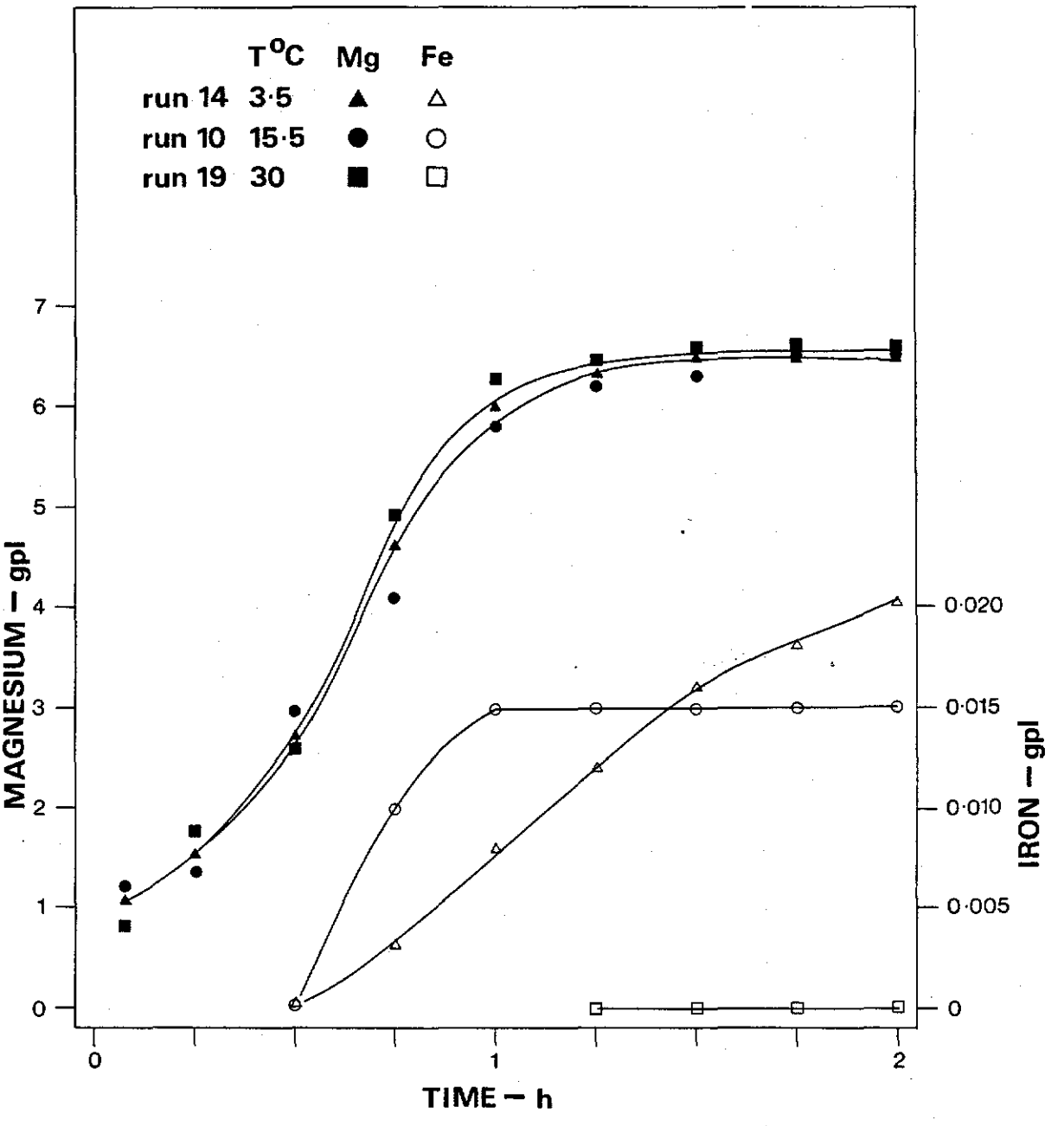

FIGURE 8. Autoclave leaching kinetic data; the effect of temperature on magnesium and iron concentration. MAG 3 calcined at 700°C for 3 h, leached at 20 g solid/litre, 0.5 h slake, 100 psig CO_2, 900 rpm. (See Table 3).

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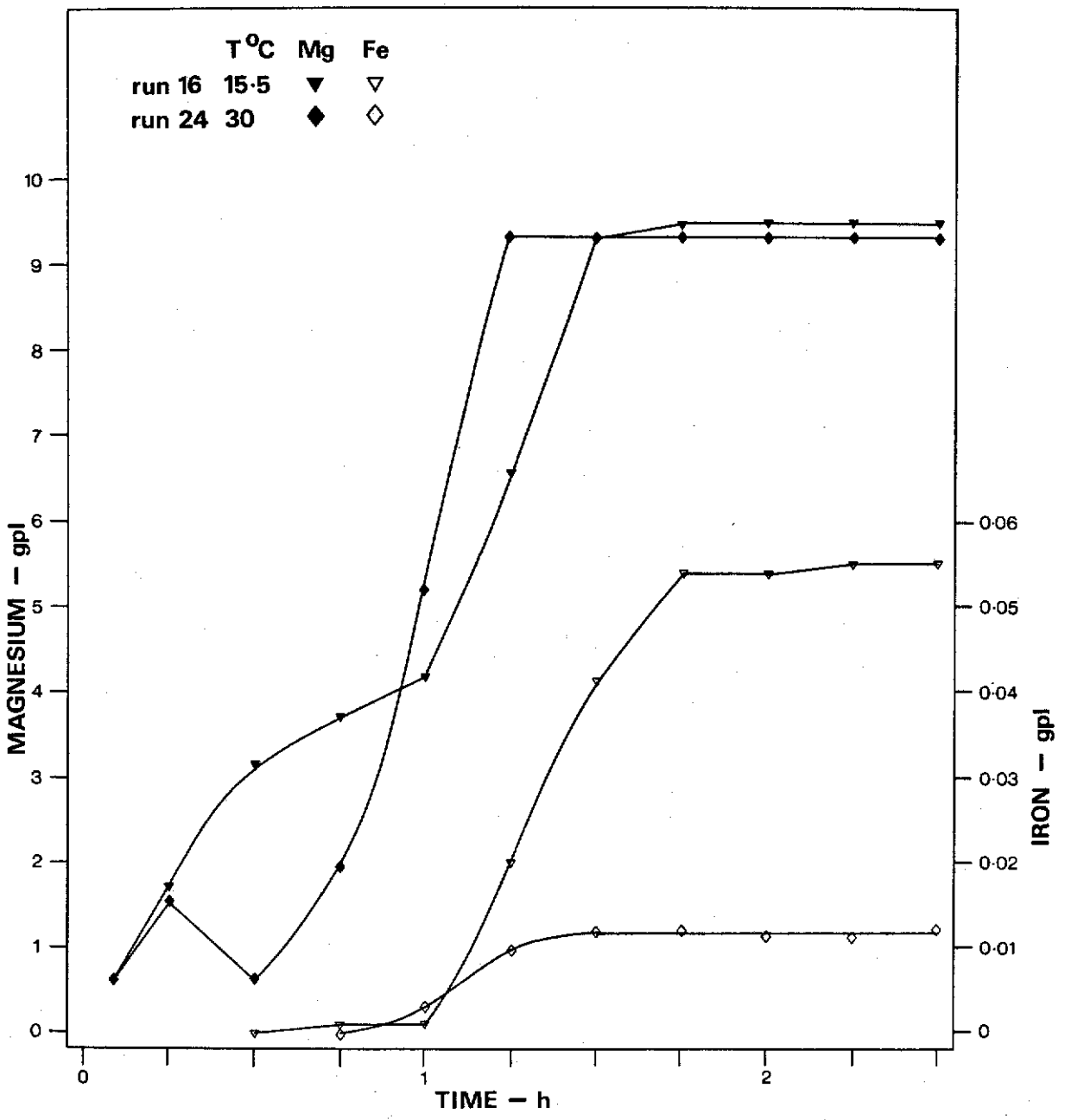

FIGURE 9. Autoclave leaching kinetic data; the effect of leaching temperature on magnesium and iron concentration. MAG 3 calcined at 700°C for 3 h, leached at 30 g solid/litre, 0.5 h slake, 100 psig CO_2, 900 rpm. (See Table 3).

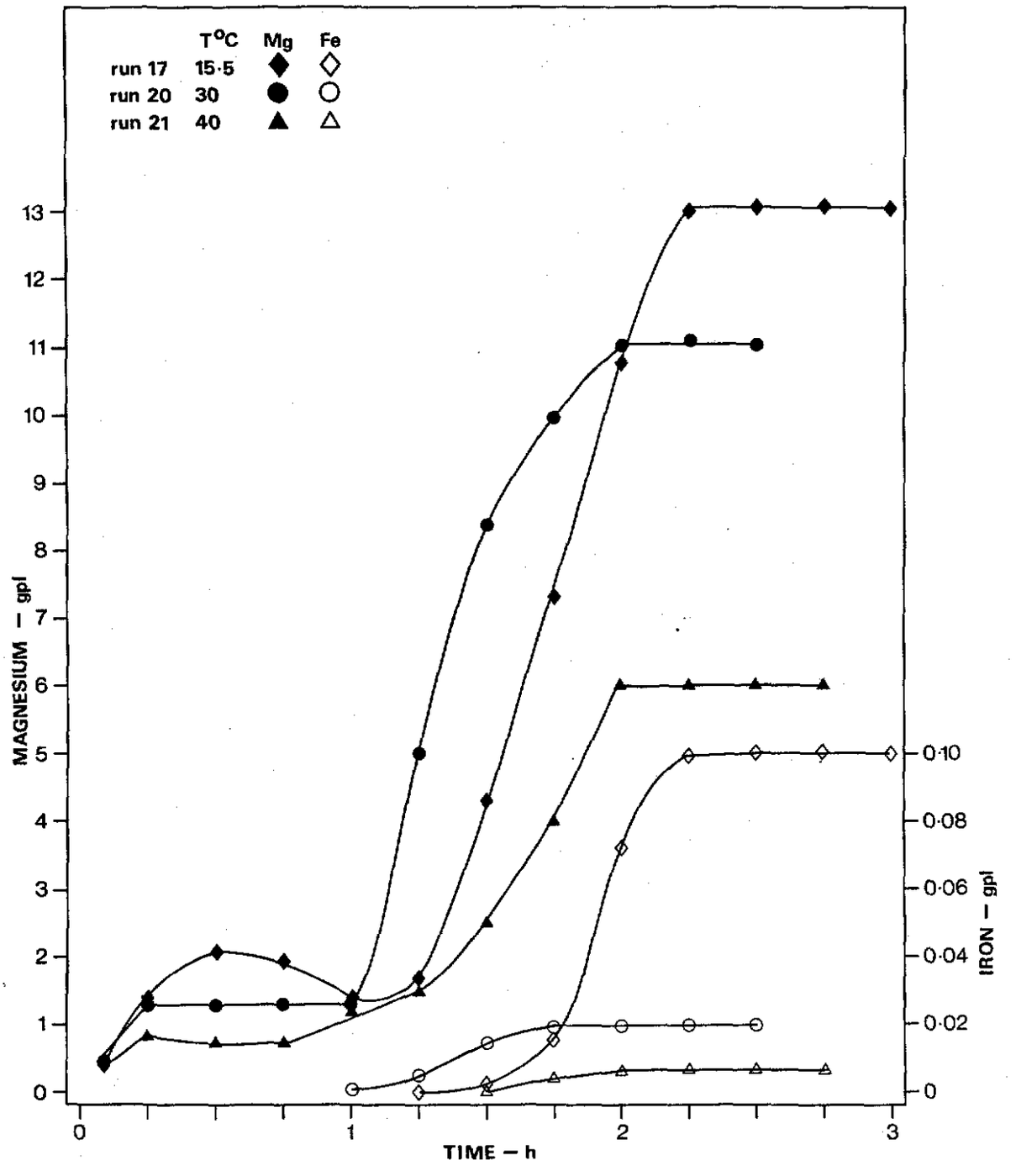

FIGURE 10. Autoclave leaching kinetic data; the effect of leaching temperature on magnesium and iron concentration. MAG 3 calcined at 700°C for 3 h, leached at 40 g solid/litre, 0.5 h slake, 100 psig CO_2, 900 rpm. (See Table 3).

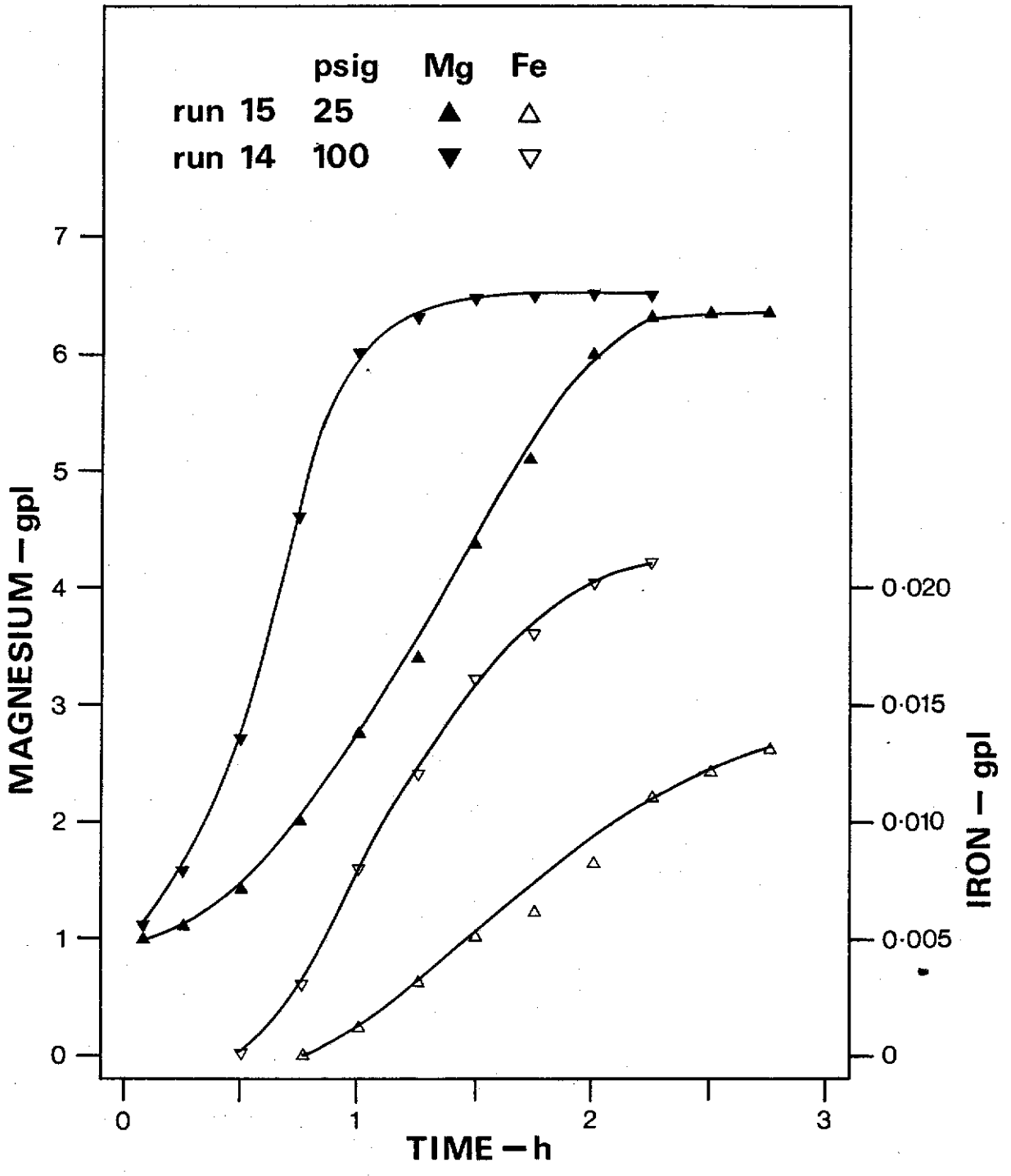

FIGURE 11. Autoclave leaching kinetic data; the effect of carbon dioxide pressure on magnesium and iron concentration. MAG 3 calcined at 700°C for 3 h, leached at 20 g solid/litre, 0.5 h slake, 3.5°C, 900 rpm. (See Table 3).

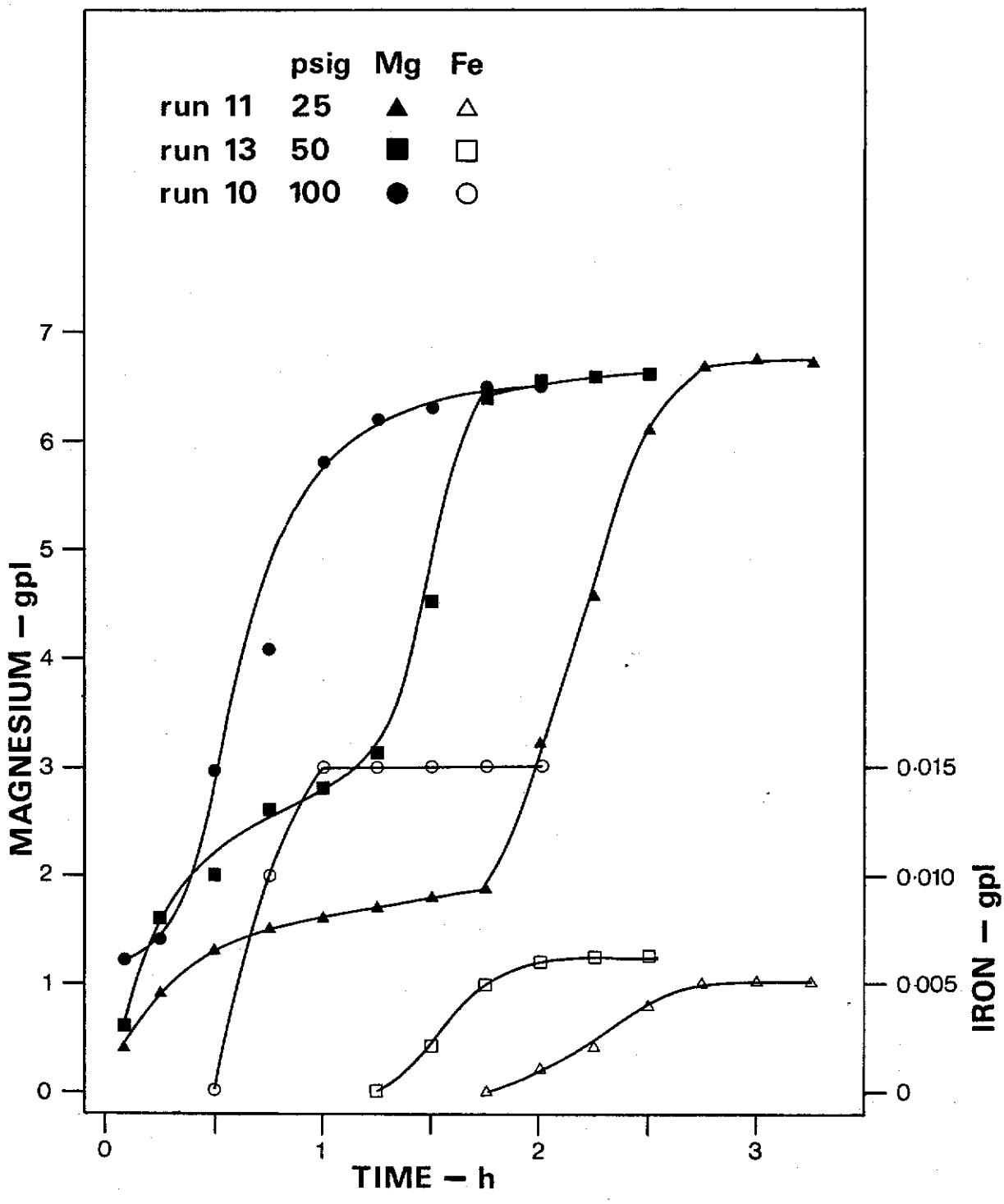

FIGURE 12. Autoclave leaching kinetic data; the effect of carbon dioxide pressure on magnesium and iron concentration. MAG 3 calcined at 700°C, 900 rpm. (See Table 3).

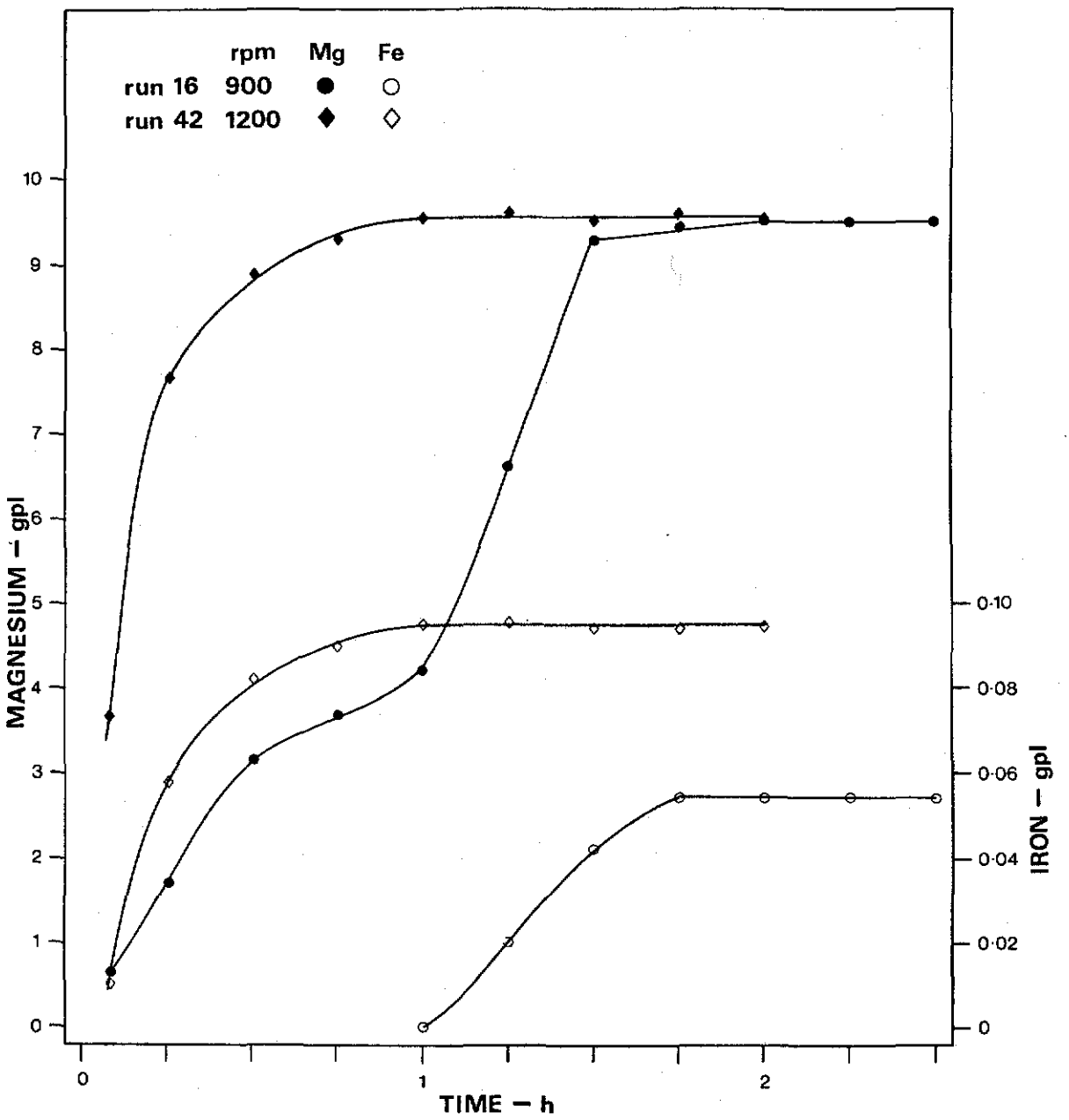

FIGURE 13. Autoclave leaching kinetic data; the effect of agitator rotation on magnesium and iron concentration. MAG 3 calcined at 700°C for 3 h, leached at 30 g solid/litre, 0.5 h slake, 15.5°C, 100 psig CO_2. (See Tables 3 and 8).

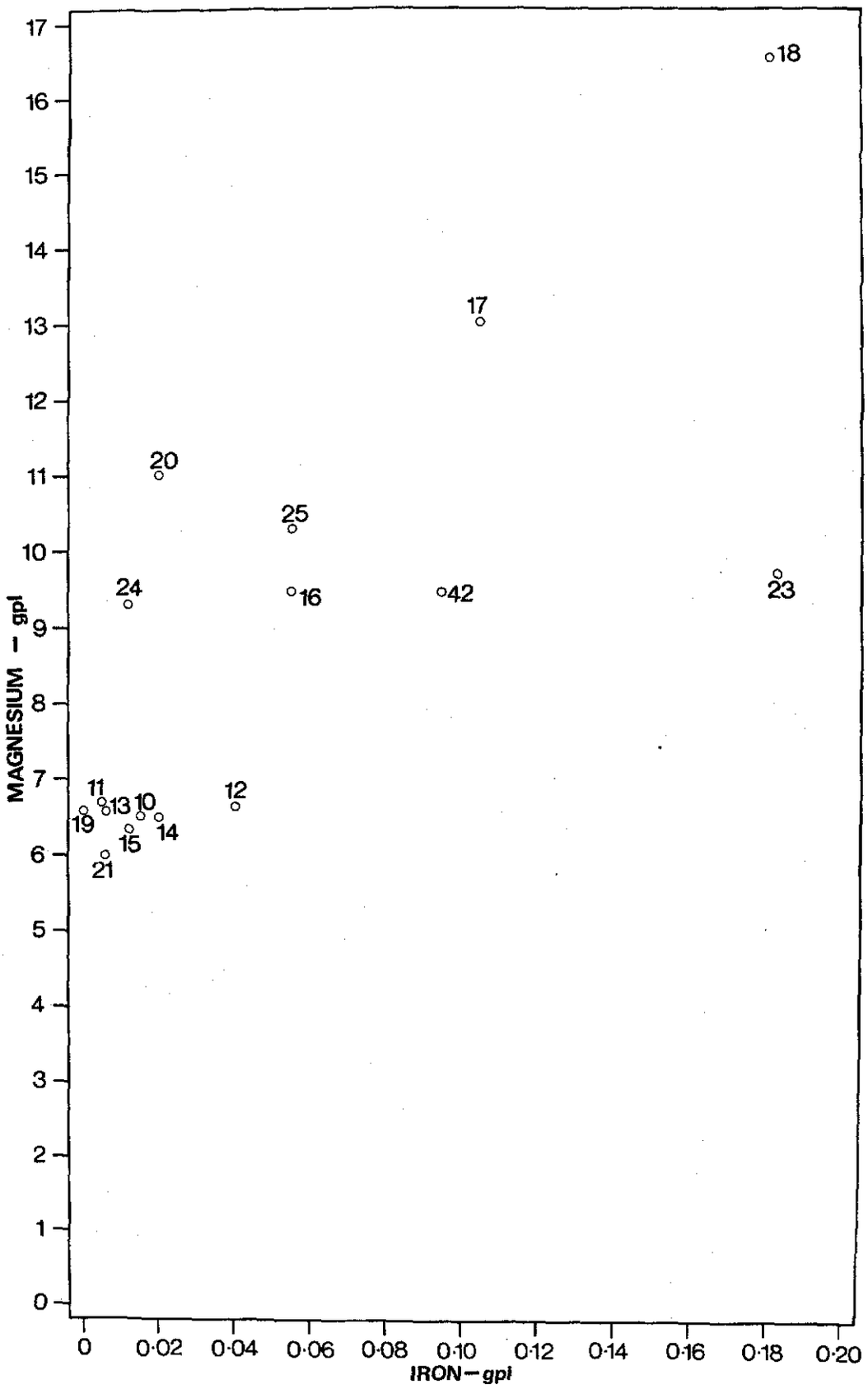

FIGURE 14. Autoclave leaching data; magnesium concentration *versus* iron concentration as a function of leaching conditions. (See Tables 3 and 8).

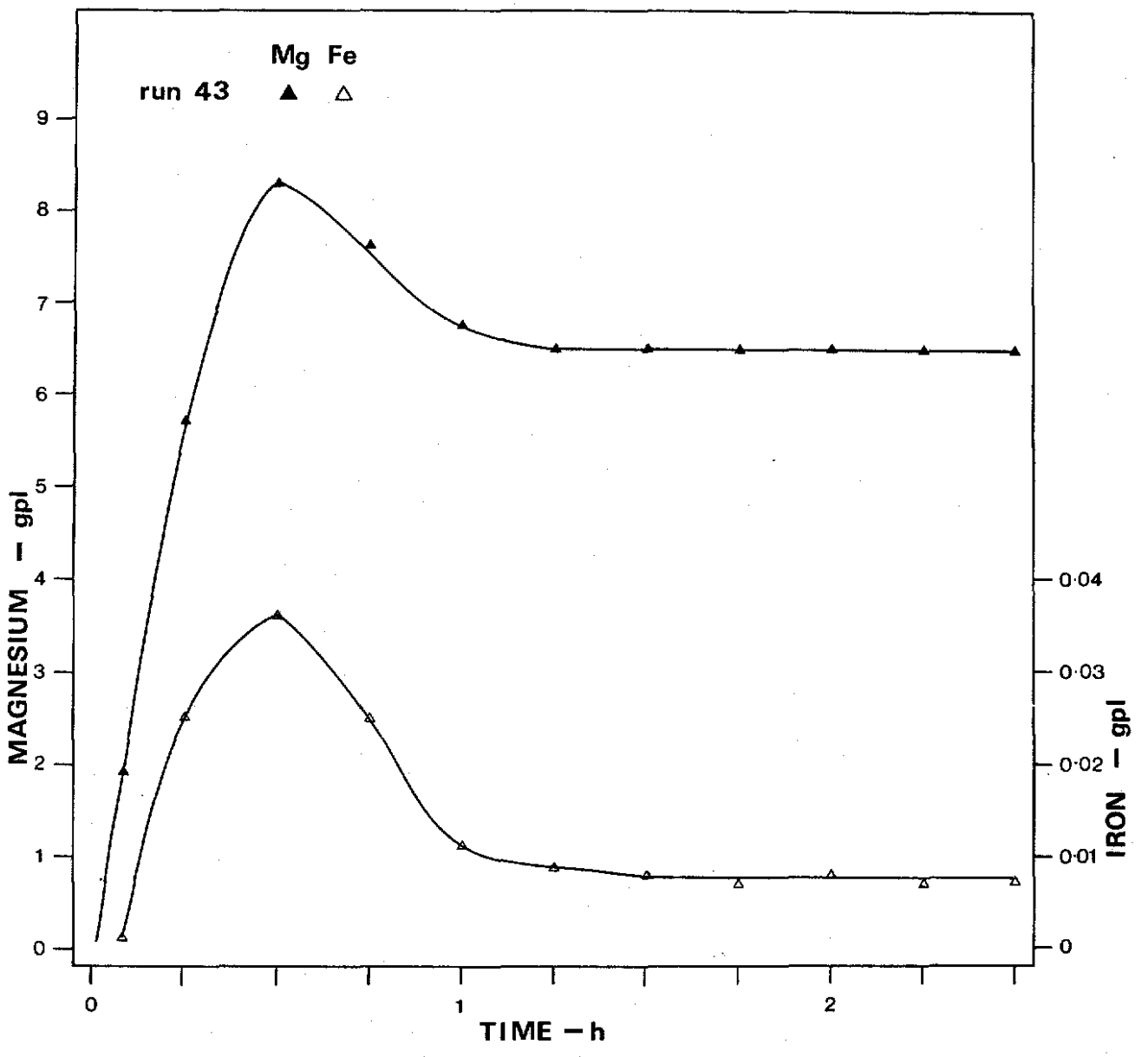

FIGURE 15. Atmospheric pressure leaching kinetic data. MAG 3 calcined at 700°C for 3 h, leached at 30 g solid/litre, 0.5 h slake, 5 ℓ/min CO_2. (See Table 9).

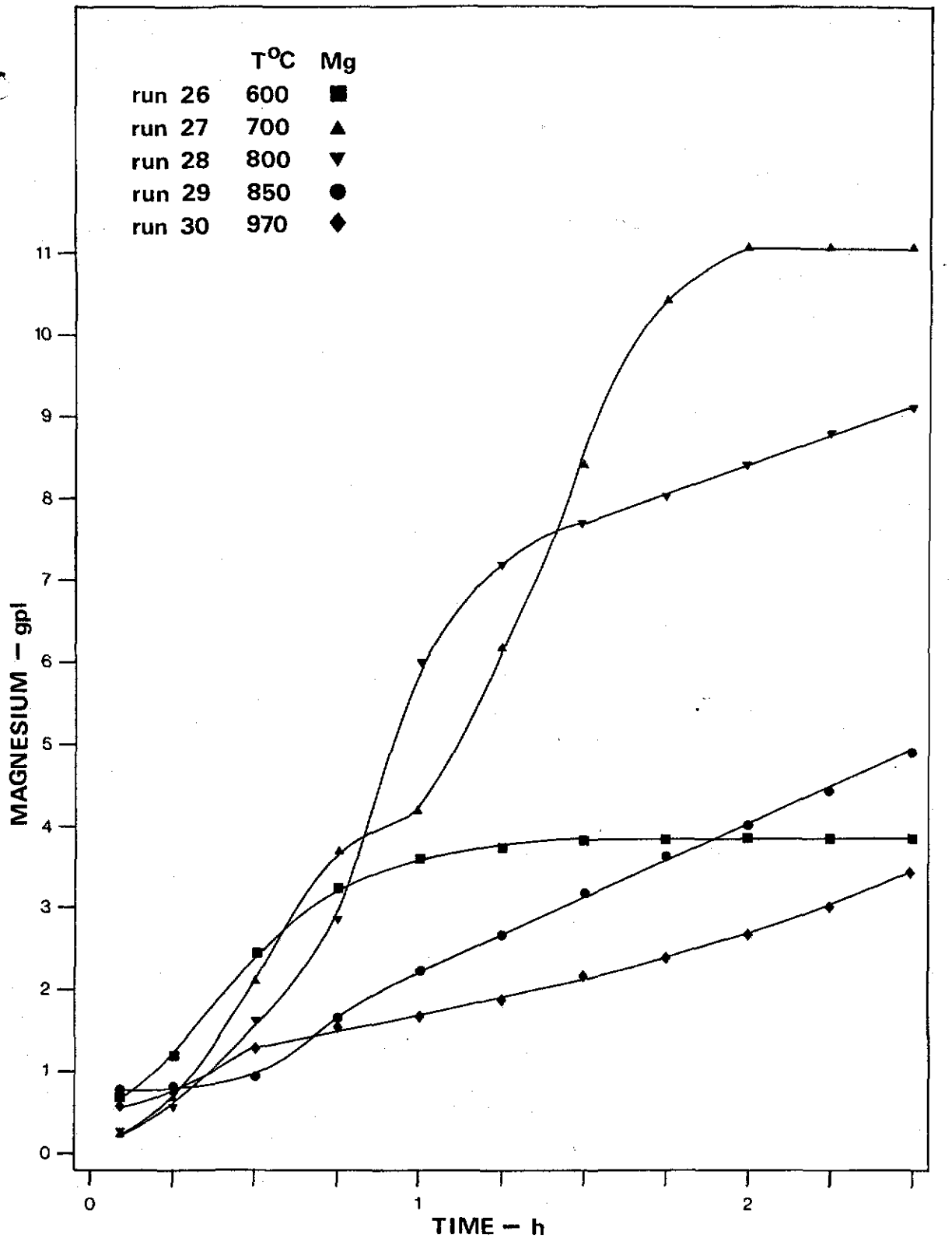

FIGURE 16. Autoclave leaching kinetic data; the effect of calcination temperature on magnesium concentration. MAG 3 calcined for 1 h, leached at 30 g solid/litre, 0.5 h slake, 15.5°C, 100 psig CO_2, 900 rpm. (See Table 10).

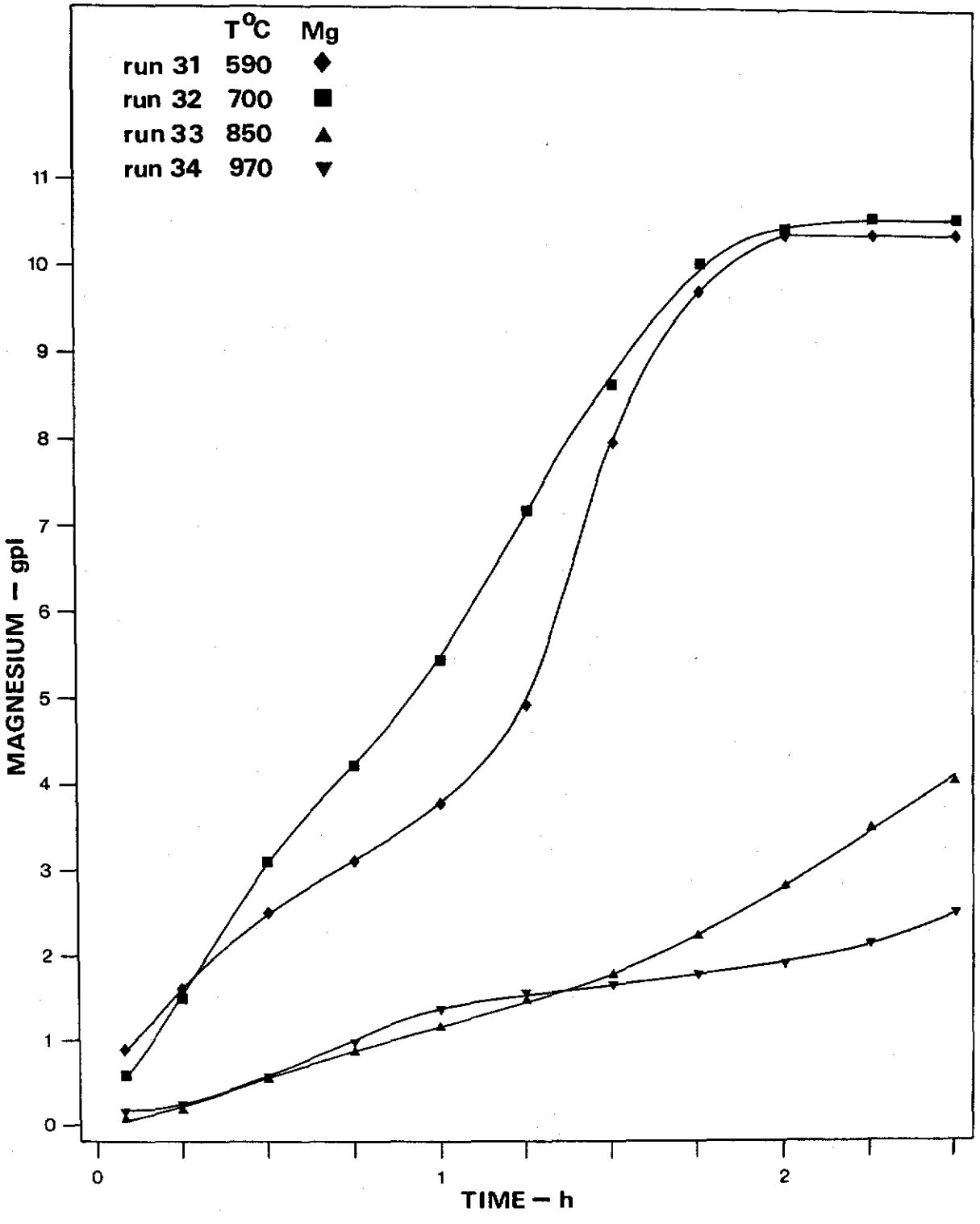

FIGURE 17. Autoclave leaching kinetic data; the effect of calcination temperature on magnesium concentration. MAG 3 calcined for 3 h, leached at 30 g solid/litre, 0.5 h slake, 15.5°C, 100 psig CO_2, 900 rpm. (See Table 11).

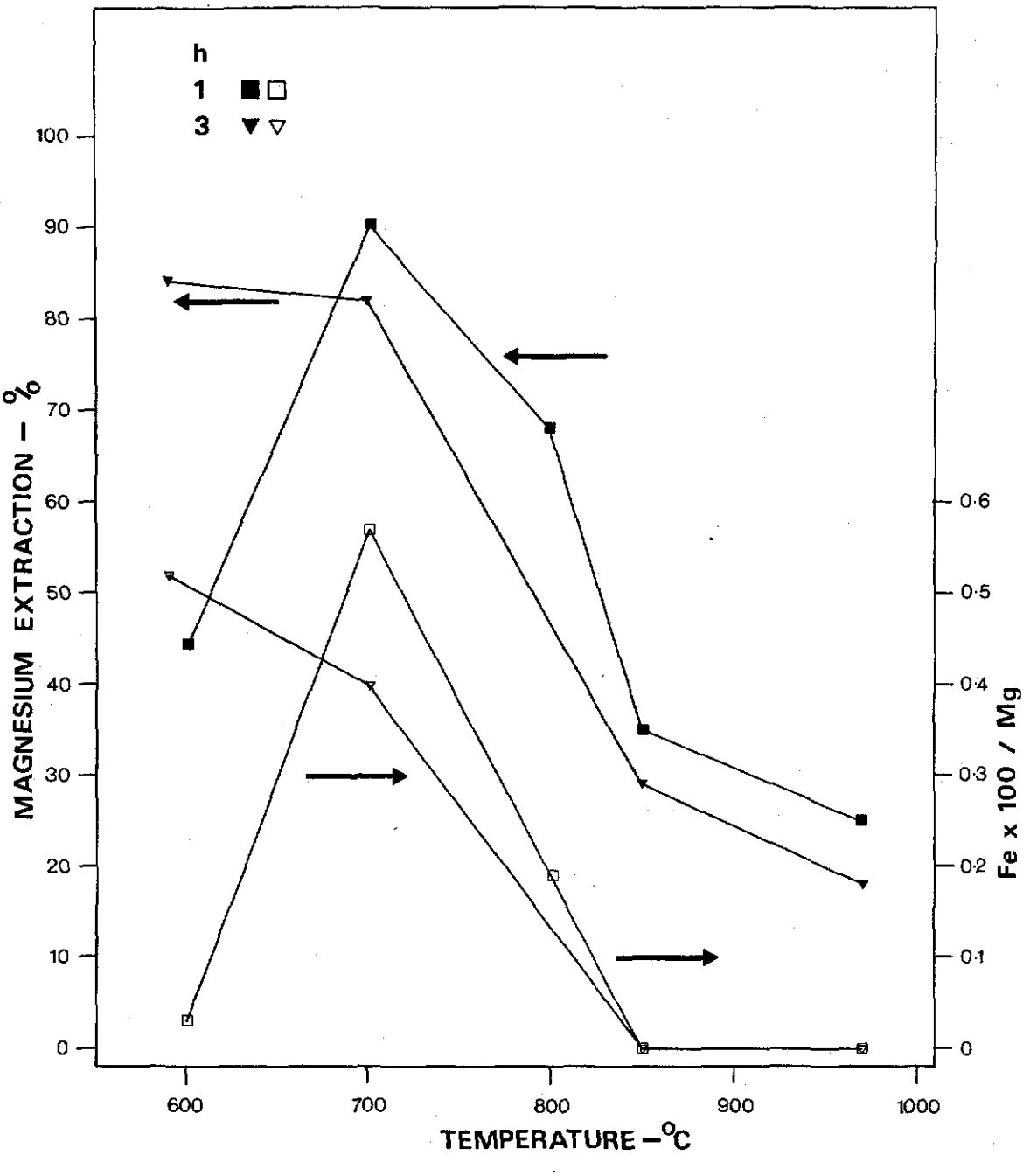

FIGURE 18. Magnesium extraction (%) and (Fe × 100/Mg) concentration ratio of pregnant liquors as a function of calcination temperature at calcination times of 1 h and 3 h. (See Tables 10 and 11).

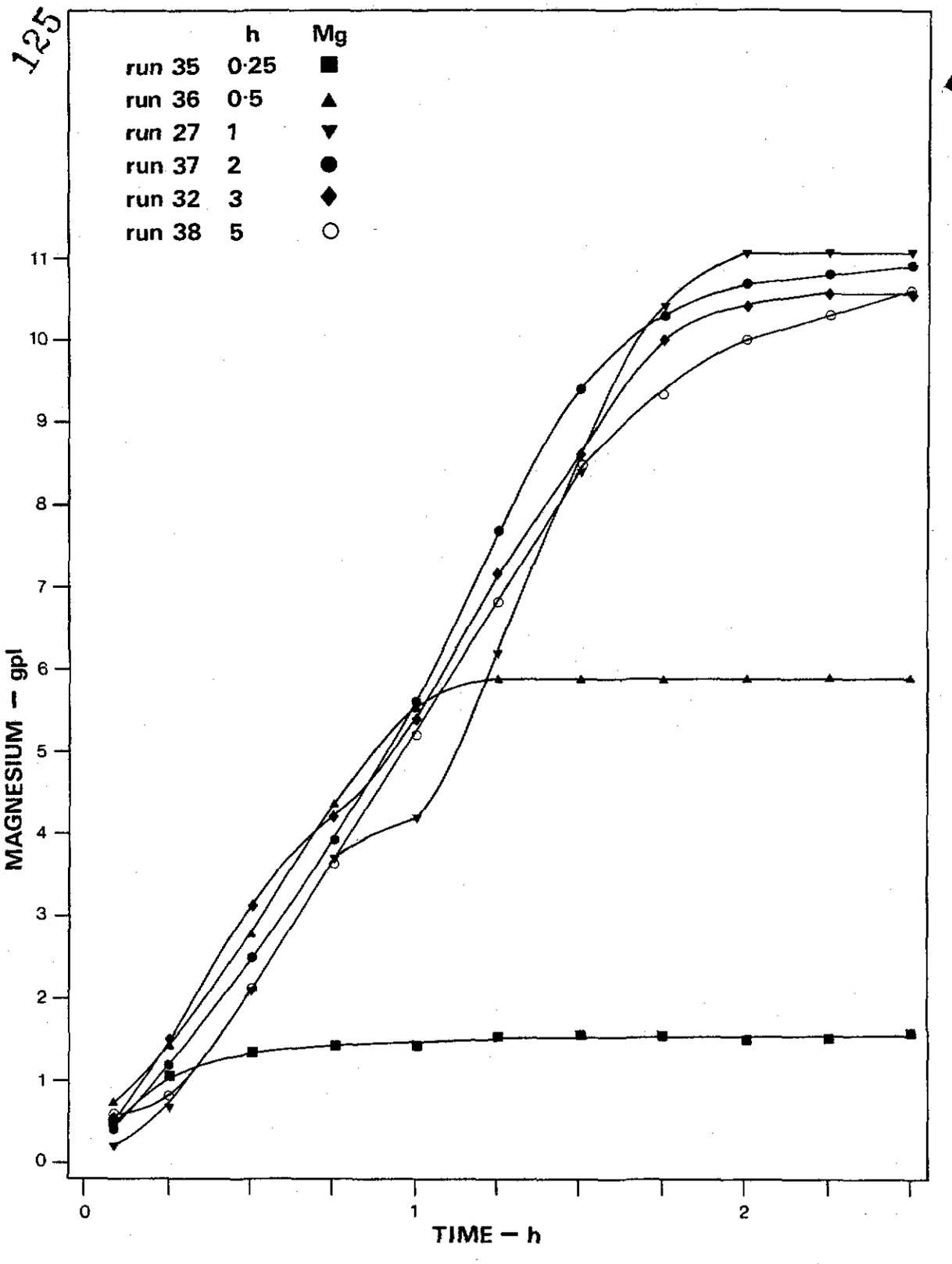

FIGURE 19. Autoclave leaching kinetic data; the effect of calcination time on magnesium concentration. MAG 3 calcined at 700°C, leached at 30 g solid/litre, 0.5 h slake, 15.5°C, 100 psig CO_2, 900 rpm. (See Table 12).

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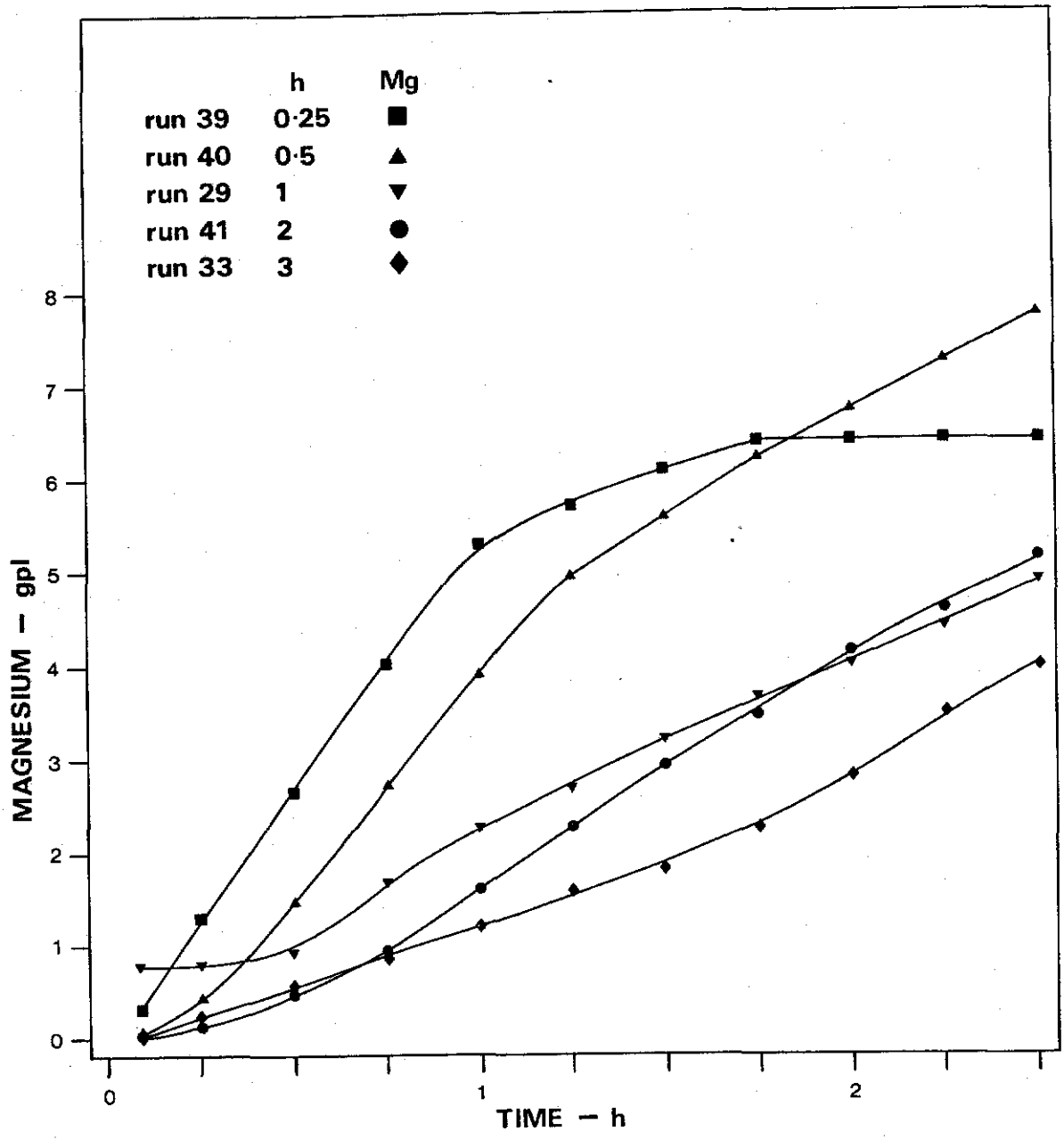

FIGURE 20. Autoclave leaching kinetic data; the effect of calcination time on magnesium concentration. MAG 3 calcined at 850°C, leached at 30 g solid/litre, 0.5 h slake, 15.5°C, 100 psig CO_2, 900 rpm. (See Table 13).

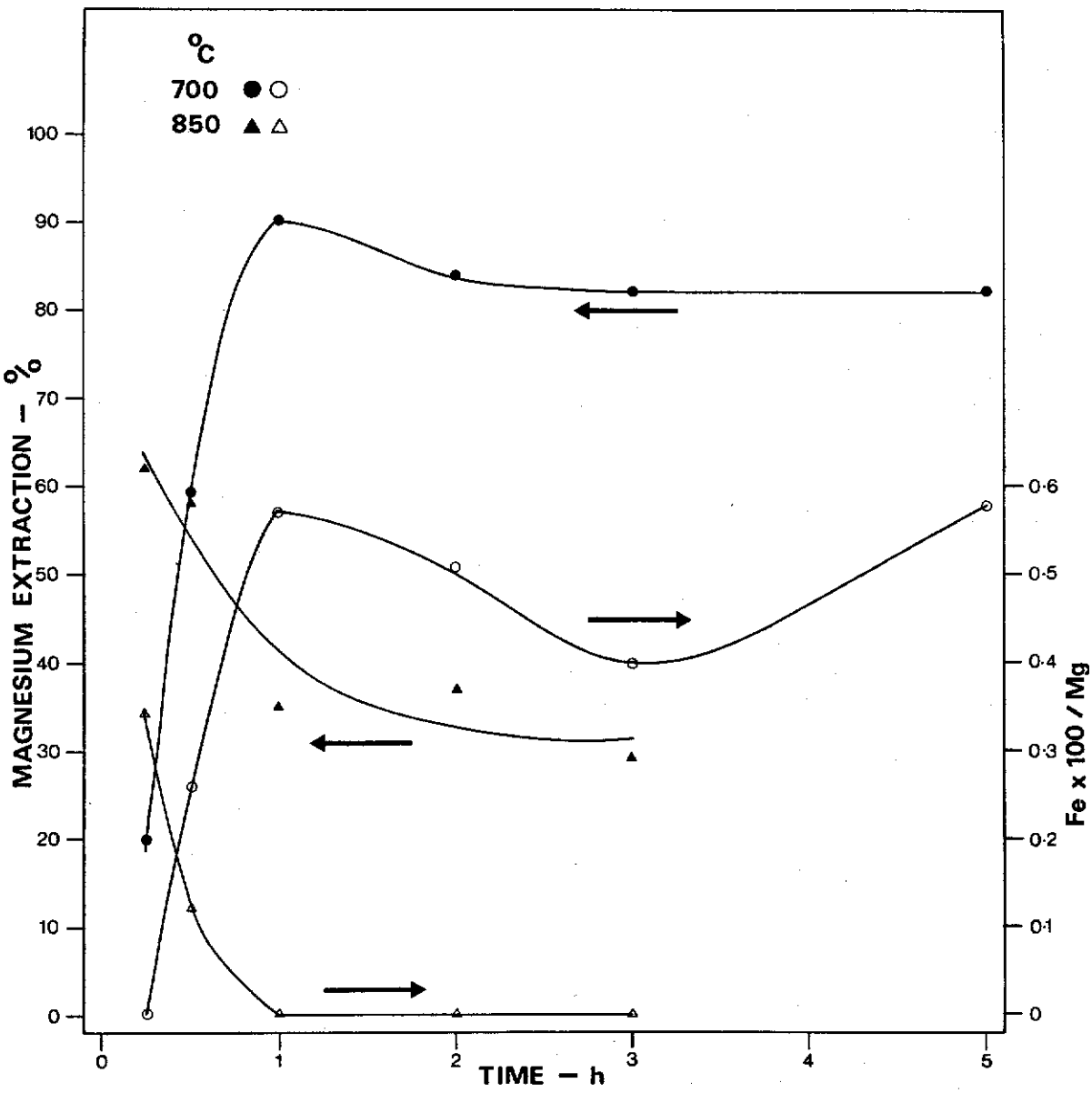

FIGURE 21. Magnesium extraction (%) and (Fe × 100/Mg) concentration ratio of pregnant liquor as a function of calcination time at calcination temperatures of 700°C and 850°C. (See Tables 12 and 13).

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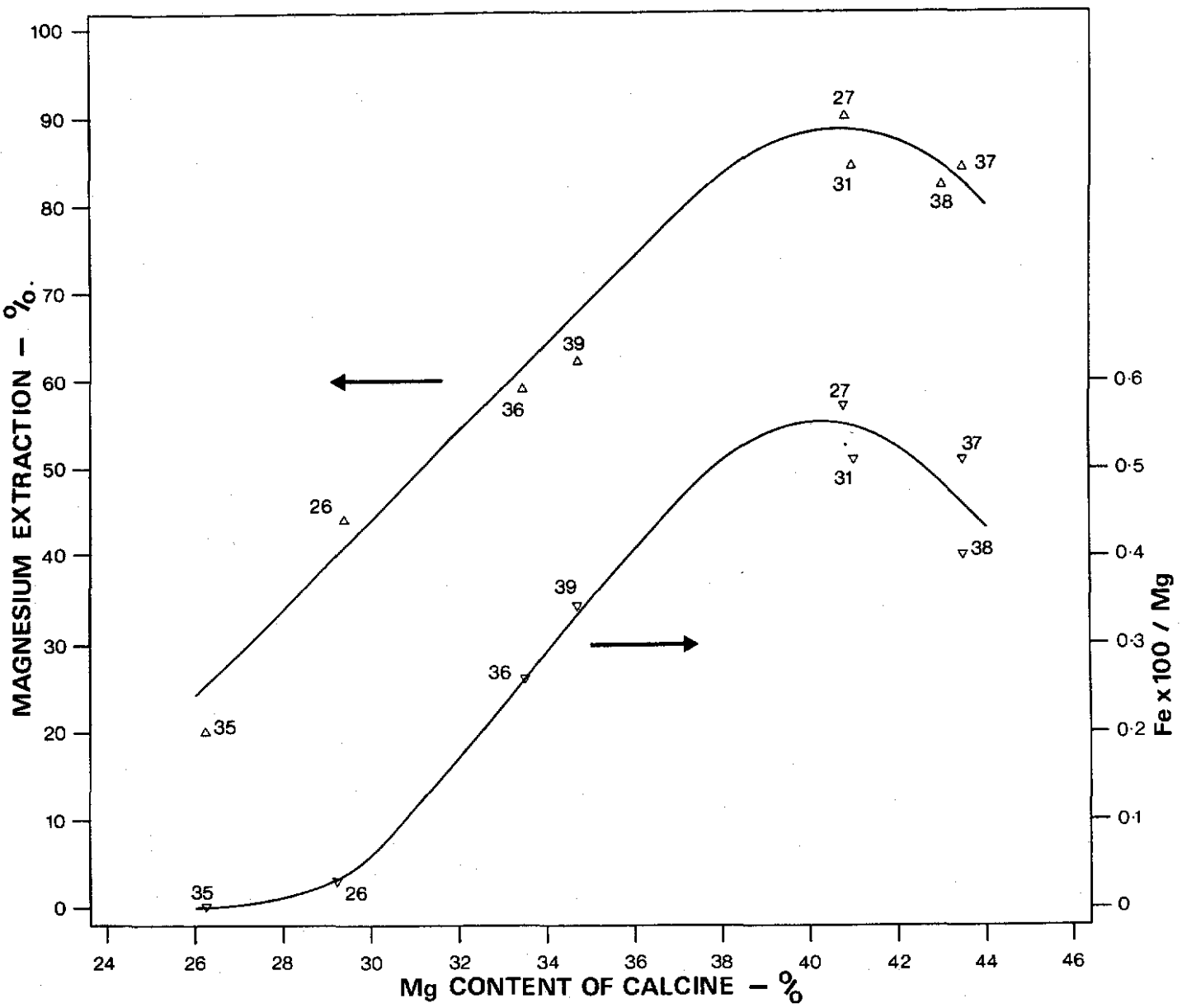

FIGURE 22. Magnesium extraction (%) and (Fe x 100/Mg) concentration ratio of pregnant liquor as a function of magnesium content (%) of calcine in test runs that have gone to completion. (See Tables 10 - 13)

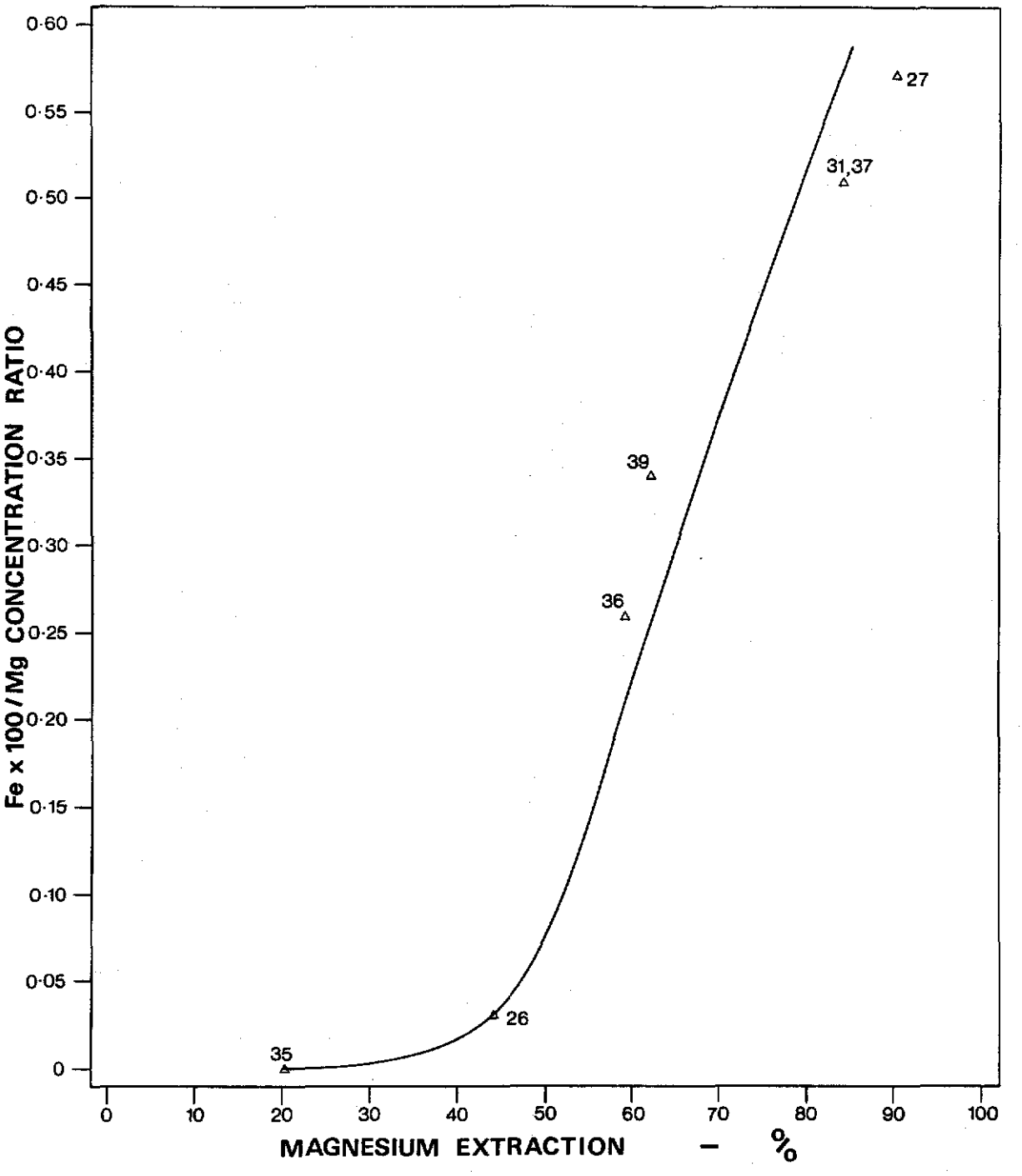

FIGURE 23. Magnesium extraction (%) as a function of (Fe × 100/Mg) concentration ratio of pregnant liquor in test runs that have gone to completion. (See Tables 10 - 13).

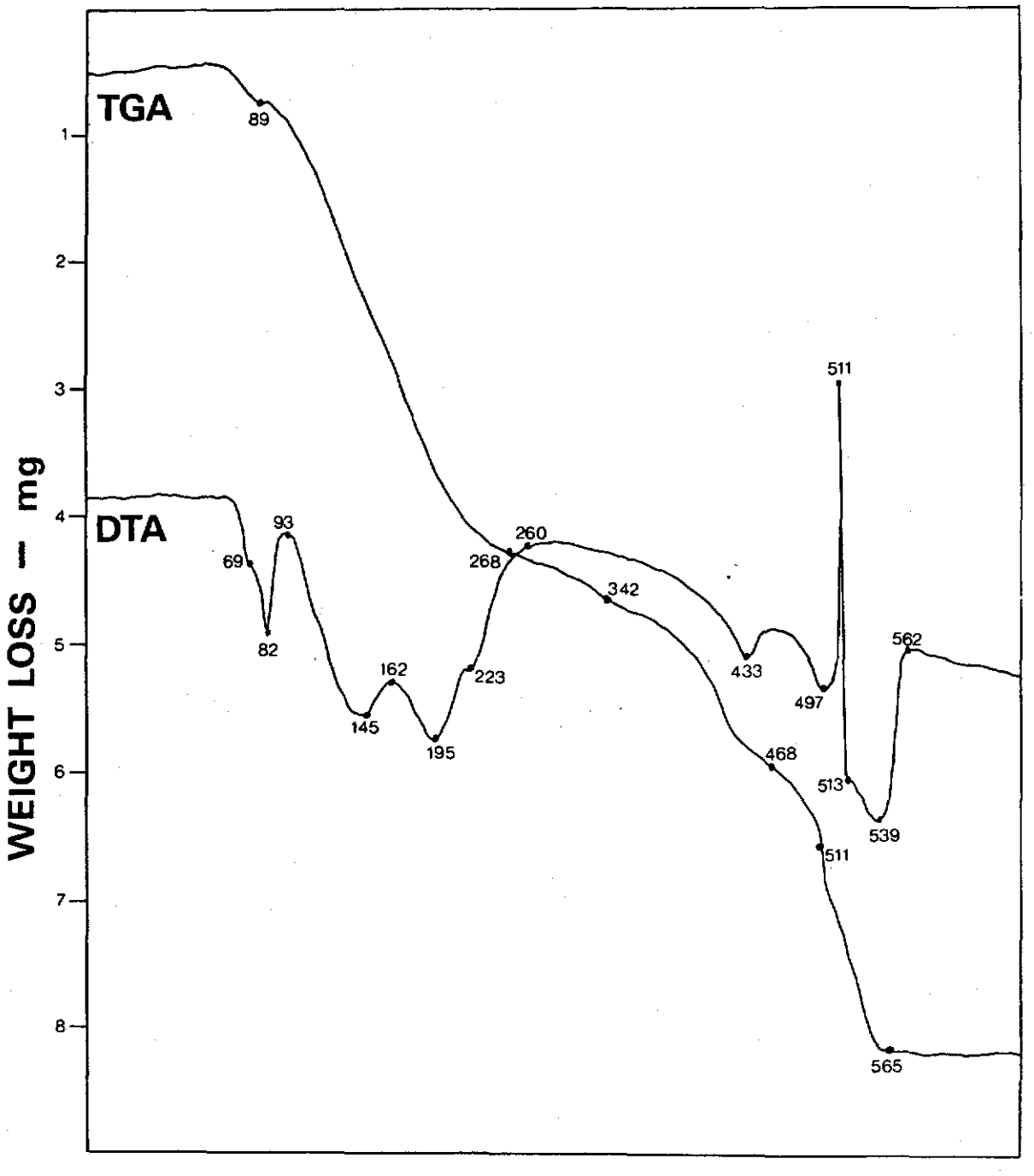

FIGURE 24. DTA/TGA curves (static air) of precipitate formed at room temperature. (Sample weight = 11.49 mg).

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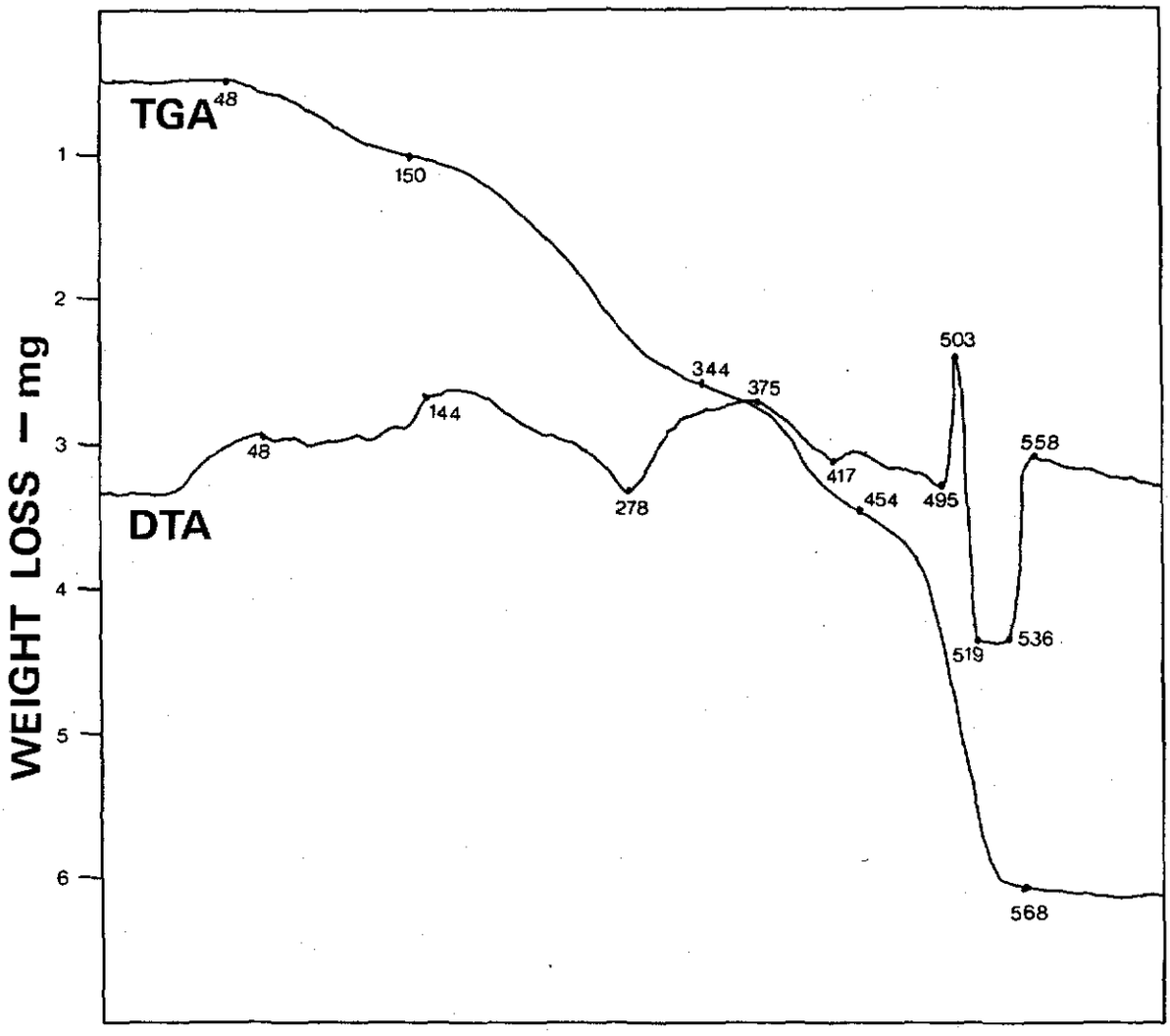

FIGURE 25. DTA/TGA curves (static air) of precipitate formed at approximately 65°C. (Sample weight = 9.26 mg).

FIGURE 26. Scanning electron micrograph showing acicular prismatic habit of nesquehonite ($MgCO_3 \cdot 3H_2O$). × 50.

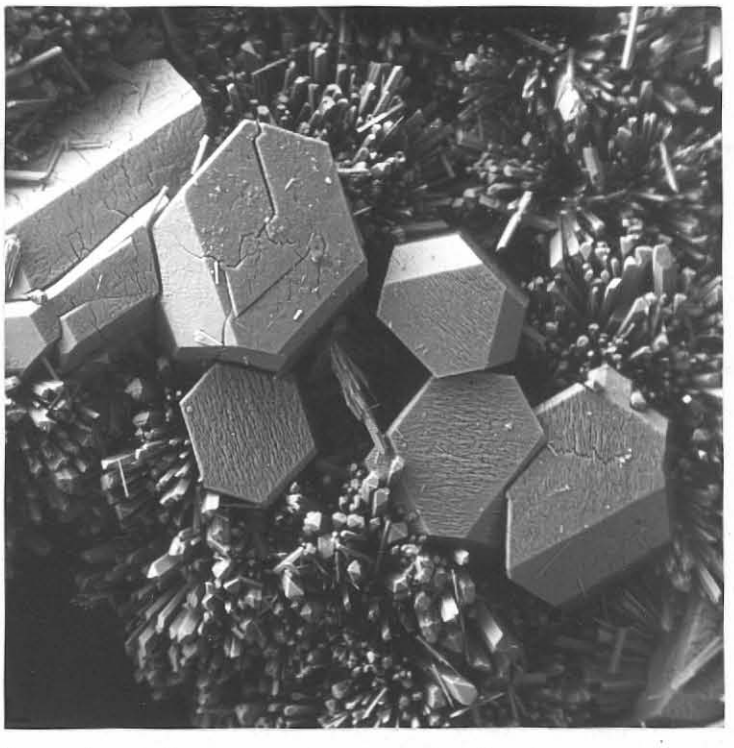

FIGURE 27. Scanning electron micrograph showing nesquehonite ($MgCO_3 \cdot 3H_2O$) and larger, short prismatic crystals of lansfordite ($MgCO_3 \cdot 5H_2O$). × 55.

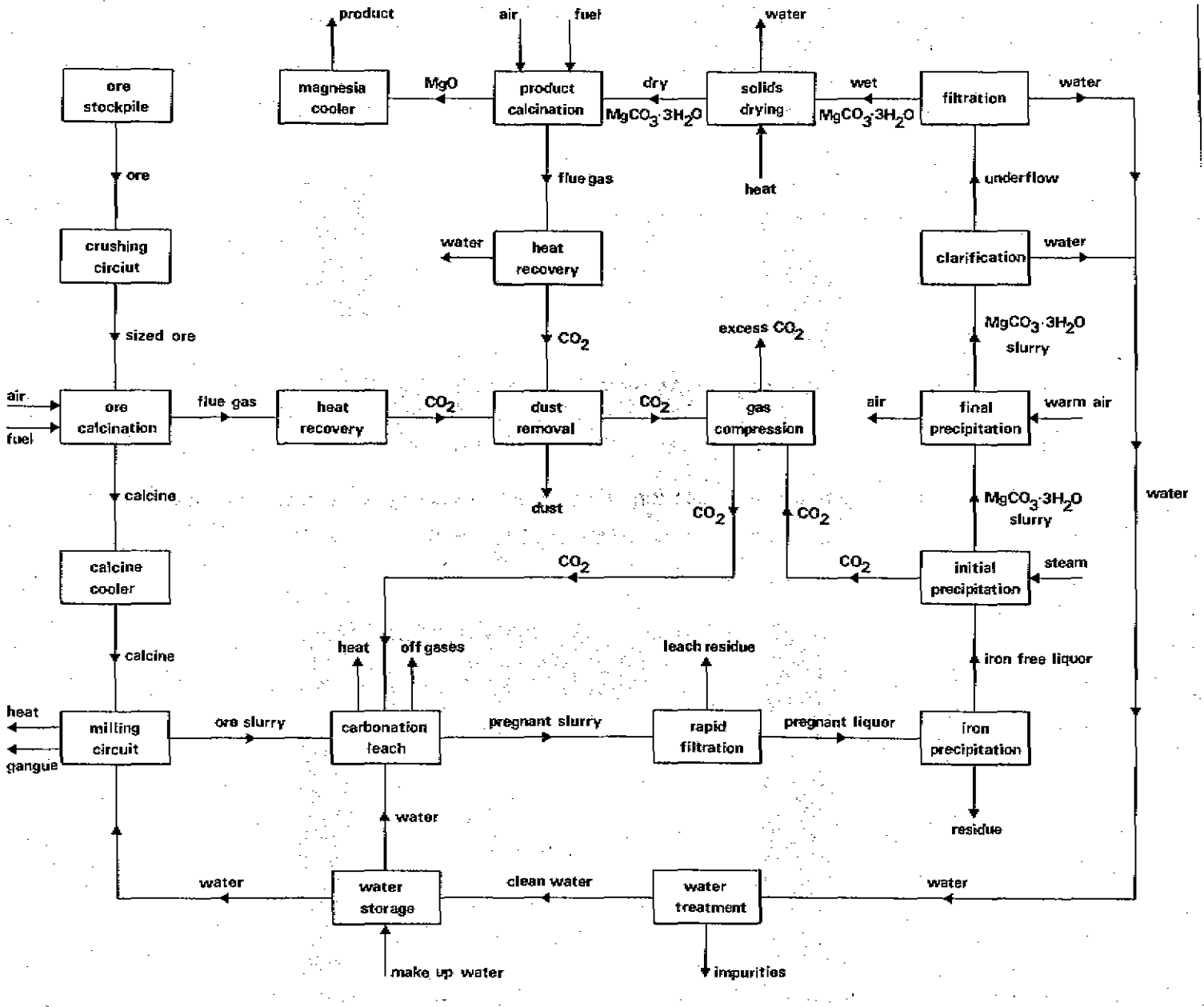

FIGURE 28. Proposed flowsheet for calcination/carbon dioxide leach process.

MCC 207

CSIRO

MINERALS RESEARCH LABORATORIES

DIVISION OF MINERAL CHEMISTRY

PRODUCTION OF REFRACTORY GRADE MgO FROM MAGNESITE

- EUROPEAN EXPERIENCE

A.F. REID

-- Mineral Chemistry Communication --

Restricted Circulation

November, 1979

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GENERAL SUMMARY - PHYSICAL AND CHEMICAL BENEFICIATION, MARKETS AND PRODUCTION

Two Austrian Companies, Veitscher Magnesitwerke Aktien-Gesellschaft, with Head Office in Vienna and research laboratories in Leoben, and General Refractories Company, European Group, Vienna, currently produce most of the deadburned magnesia and magnesia bricks and insulation (500,000 tonnes/year) used in Western Europe. They import raw or purified magnesite from Greece, Turkey, Israel and from other parts of Europe, and export 90% of their finished product.

Basse Sambre, in Belgium, also have a considerable magnesite technology, although they are not direct producers. Visits were made to the two Austrian Company Head Offices in Vienna, to the research laboratories of Veitscher Magnesit in Leoben, and the Head Office of Basse Sambre in Belgium. Brief conversations were also held with Ruthner Industrienlagen Aktiengesellschaft Vienna, who manufacture magnesium chloride spray roaster ("Amman") plant. Names and addresses of people visited are listed on page 30.

Dead-burned magnesium oxide, fired at 1800°C-1900°C to give a density greater than 3.3, and having impurity contents of a few percent to fractions of a percent is the primary product of magnesite beneficiation, purification and treatment. The majority of such material is used in refractory bricks, for which purpose it is crushed to suitable size ranges and pressed with binders into the required, frequently complex, shapes before refiring and service.

Both Austrian Companies import natural, physically beneficiated magnesite from Turkey and Greece, as well as producing from their own mines in Austria. There is a strong emphasis on physical beneficiation, preferably by heavy media methods, but also by flotation, which has been practised by the Austrians for some twenty years. Selective mining and/or selective treatment of various grades and purities is also an essential part of current practice.

Each company has an extensive experience in magnesia and chrome-magnesia brick manufacture, and a large technical back-up for this aspect of their operations.

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It is standard practice to produce a variety of magnesia product grades, ranging from the purest available, 99.5% MgO, down to 94-96% for less critical applications. Typical grades are given in Table 1.

The highest purity material is required for basic oxygen furnaces (BOF) for steel-making. The atmosphere in such furnaces is rich in CO, and FeO, Fe_2O_3 or $MgFe_2O_4$ in the bricks is reduced to Fe metal. If the Fe content is more than 0.25% this leads to local porosity, and to attack on the bricks. Boron at a concentration greater than 100 ppm also has a highly deleterious effect. Various aspects of marketing policy, world production and likely prospects are discussed below, in the description of visits to individual Companies.

European and World Production Capacities and Usage

Due to a shortage of dead-burned MgO in the early 70's a number of countries have installed new "sea-water" plants (described below). There is one in Holland, one in Ireland, and two in Italy, each of about 60,000 tonnes per year capacity. Yugoslavia and Greece (Scalistiri Company) decided not to go ahead with initial plans for these plants. Europe therefore has considerable future capacity and will probably be self-sufficient, provided the purity of the "seawater" product is high enough.

Israel has an "Amman" plant of 50,000 t.p.y., producing extremely pure material. This plant is a joint venture with the General Refractories Group, and the dead-burned product is made into bricks by this company. The spray roasters for this plant, which is described in more detail below, were manufactured by Ruthners, Vienna, who also made the pilot plant roaster for Veitscher Magnesit and are currently installing an "Amman" based plant in Yugoslavia. Thus capacity or capability exists in the European market for very high purity material as well as good standard grades.

In the U.S.A., sea-water plant (e.g. those of Harbison Walker) supply the local market, with little export, and the Steetley Company do the same for the U.K. Canadian companies also supply the Canadian market. Japan also has sea-water plants, and so has Korea, though the product is

reputedly not as pure as elsewhere. Large deposits of fairly high purity magnesite have been proved in China, which is negotiating with Austria for plant construction. European companies thus see a potential world oversupply, and the need for a very high grade product if an Australian company is to export.

Until the introduction of BOF furnaces, the consumption of relatively impure (2% to 4% Fe_2O_3) magnesia bricks was ~12 Kg per tonne of steel. This is now down to 2 or 3 Kg per tonne of high purity (less than 0.25% Fe_2O_3) magnesia. A plant producing 60,000 tonne/year of high purity MgO for BOF furnaces corresponds to about 25 million tonnes of steel. Australian production is of the order of 8 million tonnes, that of Japan about 110 million. Considerable amounts of MgO are used in situations other than BOF, but this has to be the primary market which enables the remainder of mined production to be sold.

SUMMARY OF MAGNESITE BENEFICIATION PROCESSES

1. Physical Beneficiation

Physical beneficiation by heavy media or flotation methods is preferred if the final grade is high enough, and might also represent part of the processing operation for an Australian mine, either to give relatively pure grades as a saleable product along wich chemical beneficiate or, less economically, to give a preclean to material going to a chemical plant. Selective mining for the material going to the various product grades would obviously be preferable.
More details are given on page 8.

2. Seawater Process

Dolomite or dolomitic magnesite is calcined to caustic (slakeable) condition, then repeatedly washed with seawater to take $CaCl_2$ into solution. There is a requirement of 40-70 tonnes of water per tonne of MgO. MgO. The $Mg(OH)_2$ product is calcined to MgO, briquetted and dead burned. The Fe_2O_3 content of the primary dolomite must be sufficiently low, and boron impurity can be a problem. (See last ref., p.32, for other versions.)

3. Magnesium Bicarbonate Process

This has apparently only operated intermittently since 1950 at about only 10,000 tonne per year, due to problems with final purity and the lightness of the MgO made from the intermediate product, hydrated magnesium carbonate. This last objection can probably now be overcome, by use of the prefiring and briquetting techniques used for the Israeli Amman product or sea-water products, both being $Mg(OH)_2$.

The process is presently being re-investigated in the Division of Mineral Chemistry, CSIRO. It requires calcination of magnesite to semi-caustic stage, dissolution in water by means of CO_2 injected at 2-5 atmospheres, filtration of impurities and reprecipitation of hydrated magnesium carbonate.

The relatively reactive product requires firing to remove water and carbon dioxide, possibly in a two-stage furnace or fluid bed reactor to allow CO_2 recovery. (Sensible heat left at the H_2O removal stage would not be lost.) The material would then be briquetted, and dead-burned.

4. Israeli "Amman" Process (Dead Sea Periclase).

$MgCl_2$ brine is spray roasted at 600-700°C to give MgO plus HCl and steam. The wet HCl vapour is subsequently scrubbed to 20% HCl solution and use in the production of phosphoric acid. The MgO product contains unreacted $CaCl_2$, which is removed by washing to give very low residual CaO, and a very high purity product, Table 1. The slaked MgO, i.e. $Mg(OH)_2$, is fired to remove water, briquetted and dead burned. This plant is a joint venture with General Refractories Group, who market the product. The spray roasters, 2 x 25,000 tonnes per year, were supplied by Ruthner, and are illustrated in a Company brochure, p.32.

5. Magnesite-Hydrochloric Acid Route

In this process, pilot planted by Vietscher Magnesit, calcined or partly calcined magnesite of >90% and preferably >95% $MgCO_3$ content is dissolved in 20% HCl solution. In subsequent stages, iron, aluminium and silica are co-precipitated and filtered off, H_2SO_4 is added to precipitate $CaSO_4$ which is filtered off, and the resulting brine fed to an

Amman spray roaster. The product, very high purity MgO, Table 1, is ∿1 micron mean size. This material is briquetted, possibly partially prefired, and then dead burned. Veitscher Magnesit hold extensive patents on the various chemical stages (see page 32).

The Amman roaster of their pilot plant was supplied by Ruthner, p.32, who also offer a version of the front end chemical stages, and are supplying a plant to Yugoslavia. In their version, the calcium precipitation stage is omitted, and the product MgO is washed free of unreacted chlorides ($CaCl_2$ and any NaCl, KCl etc. present) as in the Israeli operation. This is perhaps simpler, and gives a product free of CaO etc., but involves slaking of the MgO to $Mg(OH)_2$ and its subsequent dehydration.

SUMMARY OF CHEMICAL BENEFICIATION ENERGY AND PROCESS REQUIREMENTS

All of the chemical processes require at least two, and in some cases three, calcination steps, and extensive water washing or solution treatments. Reputedly the sea-water and hydrochloric acid routes have comparable final requirements, Table 2, with the latter probably somewhat higher. According to the Austrian companies, the bicarbonate route is even more expensive of fuel. This may not actually be so and current CSIRO research may also reduce the energy requirements.

CAPITAL INVESTMENT COSTS

All of the chemical beneficiation plants will be relatively capital intensive. For example, the Netherlands plant, 1979, cost 150 million guilders, or 68 million dollars, for a 50,000 or 60,000 tonne/year MgO capacity, based on rather impure dolomite.

For the Ruthner version of the hydrochloric acid route the chemical plant cost (quoted by Ruthner, October 16,1979) is $21.5 million for 25,000 tonnes per year, plus 60-70% for civil works etc., leading to $35 million for 25,000 tonnes. For 50,000 tonnes, civil works costs per unit may be expected to be less, say 50% on $(2 x 21.5) million, or $65 million for 50,000 tonnes/year.

TABLE 1. CHEMICAL COMPOSITION OF VARIOUS GRADES OF MgO

Impurity	Required for BOF bricks	Israeli Amman Plant	Veitscher-Magnesit Pilot Plant	Good Natural Grade after physical beneficiation		Sea-water Plant
				General Refractories	Veitscher	
Fe_2O_3	<.5% combined pref. lower	300 ppm	300 ppm	0.25 - 0.5%	0.7% [a]	∿0.25% combined
Al_2O_3		-	-			
CaO	< ∿1%	Sometimes added or up to 0.5% present	up to 1.0%	< 0.8%	1.5 - 2.0 max. 3.0%	b
SiO_2	.4%, pref. < 2	300 ppm	300 ppm		0.8 - 1%	b
CaO/SiO_2	> 2					
B or B_2O_3	<100 ppm		∿< 10 ppm			Not always met
Grade		∿99.9 → 99.4%		97.0%		
(Density)	(>3.3)					

(a) If magnesite originates in serpentine Fe is very low. (b) Not stated.

TABLE 2. PLANT ENERGY COSTS PER TONNE DEADBURNED MgO, EXPRESSED AS Kg OF HEAVY FUEL OIL

(1 Kg fuel oil ≡ 42.5 megajoule)

	Fuel Kg/tonne	Water throughput per tonne of MgO tonnes	Information Source
Natural Magnesite	200	-	Dr. Longin[a]
Seawater	750-1000	40-70	Dr. Longin[a]
Veitscher Magnesit $MgCl_2$ route from magnesite	∿same as seawater 1200	∿10	Dr. Grill Dr. Longin[a]
Ruthner $MgCl_2$ route from magnesite	900[d]	10	Ruthner I.A.[c]

[a] General Refractories Group

[b] Veitscher Magnesitwerke-Aktiengesellschaft

[c] Ruthner Industrienlagen Aktiengesellschaft

[d] Plus 900 kWh/t electric energy plus 30% on energy and electricity for "manpower and maintenance", giving about 1200 Kg/tonne overall, in agreement with Reference (a).

DETAILED INFORMATION FROM COMPANY VISITS

BASSE SAMBRE, DR. S. MARKOVIC, AUGUST 1979

Basse Sambre are primarily a design consultant firm who specialize in mineral beneficiation by heavy media and in materials handling. They have extensive experience in sinter plant for iron ore; in the materials handling aspects of iron ore; in heavy media beneficiation of coal, magnesite and other minerals, and possibly have a number of other activities which we did not discuss. Their offices are located at Moustier-sur-Sambre, a small town in Belgium which is half-way between Charleroi and Namur. It can be readily reached by train from either place.

Dr. Markovic is in charge of engineering implementation for mineral beneficiation. He discussed at length the requirements for the beneficiation of magnesite and also applications of heavy media separation to the concentration of tin ores. As background, he mentioned that the iron ore which is smelted in Belgium comes in part from Lorraine, but the greater part from overseas, including Brazil and Sierra Leone. It is unloaded at Antwerp, some of it directly on to barges and some into stockpiles for reclamation. Basse Sambre have designed much of this equipment, including the sampling equipment necessary to determine the grade and the stacking and mixing sequences for the unloaded ore. Much of this ore is shipped inland, e.g. to Charleroi, by barge.

Dr. Markovic offered to give any assistance, either in the way of publications of opinions, on our future magnesite operations and would be a very valuable person to keep in touch with.

Physical Beneficiation of Magnesite by Heavy Media and Flotation

The methods which Basse Sambre use in magnesite beneficiation are primarily those of heavy media separation. Either the material is separated from the lighter gangue phases such as silica, and possibly calcium silicates, which float while the denser magnesite sinks, or if the magnesite is not in a condition where this is possible, e.g. if it is highly porous, the opposite technique is used. It is common to heat

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the magnesite to, say, 450° which partly or completely decomposes it while still retaining the original lump structure without any recrystallization. This material is then much less dense than the original and can be floated while allowing heavy impurities such as magnesium silicates or calcium silicates or in fact unreacted dolomite or calcium carbonate, to come out in the heavy fraction. If this course is pursued, there is usually a precursor heavy media separation where the lightest impurities, less than density 2.6 for example, are floated off to give a preliminary clean.

If dolomite is physically intergrown with magnesite a temperature of 650°C decomposes the dolomite to calcium oxide and magnesium oxide and the calcium oxide can be slaked and washed out. Some magnesium hydroxide is formed during this operation but the magnesium lumps remain coherent. The hydroxide content can be removed during subsequent dead burning.

Thus the steps in sequence would be:

1. A heavy media separation in which magnesite in the original form is allowed to sink and light gangue is floated off.

2. Causticization at 450°, or 650° if dolomite is present, followed by washing or agitation in order to convert calcium oxide from the dolomite to calcium hydroxide which in fine form can be washed out.

3. The product is then passed through heavy media separation again, this time of density to allow the magnesite which is partially porous to float and the dense impurities, for example ferrugenous dunite (magnesium iron silicate), to sink.

This overall procedure gives a material which is better than 97% MgO when finally fired. The samples which Dr. Markovic showed me, which had been purified via such a procedure, were extremely clean and white and had very low iron content. Heavy medium separation is preferred to flotation because it is generally cheaper and can give magnesite in lump form suitable for firing and avoids the need for the subsequent compaction which is required when material is fine. However

its use leads to some losses in fines which may be either stockpiled or put to a flotation treatment. Flotation should only be applied when the product obtained is going to be of good grade and of good yield, otherwise it is not worthwhile.

In physical beneficiation it is desirable to give selective treatment on the basis of particle or lump size. Thus for some sizes heavy media separation gives an adequately pure product. The fines may be discarded or treated by flotation and the larger pieces may be causticized and retreated to remove calcium oxide and give a product which can be finally cleaned by floating rather than sinking. A careful selection of treatments for the various size ranges can result in a final blended product which is much better than can be obtained by a single treatment for all sizes.

There is also considerable South African experience in heavy media separation and in washing causticized magnesium carbonate free of calcium content. (Mitchell Cotts Group, Frazer and Chalmers, S.A.). In some cases, washing out of CaO is sufficient without further heavy media treatment.

The heavy media equipment which Basse Sambre have developed consists primarily of a trough with controlled flow and with a magnetic "valve", operated by means of a coil. The electrical current in the coil regulates the magnetic intensity in the orifice through which the magnetic media flows. The valve contains no mechanical or moving parts and acts purely by the action of the magnetic field on the magnetic medium. Using this equipment it is possible to perform heavy medium separation on size ranges down to approximately 1 mm, rather than stopping at about 12 mm as is common in some practices. However, it may be necessary to make a cut-off at about 3 mm, depending on the density or porosity of the material. It was emphasized that it is necessary to get a very sharp density cut, without turbulence in the bath, in order to achieve the necessary separations with material such as magnesite. It is possible to carry out heavy media analysis in the laboratory and by using suitable plots determine the expected efficiency of a larger scale operation.
Heavy media can be simulated with bromoform or diluted bromoform or other mixtures of suitable specific gravity, namely in the range 2.3 to 3.

Such problems such as wetting are encountered if the material is porous but if it is densely crystalline, such as the Savage River material appears to be, then there should be no problem in transferring the results from bromoform and similar liquids to those which will be obtained with ferro-silicon media.

Assessment of Savage River Magnesite for Physical Beneficiation

It would seem to be important to establish the heavy media characteristics of the Savage River magnesite and possibly also to carry out tests using flotation. We should also determine whether the material is crystalline or crypto-crystalline and performs some flotation tests on material down to say 100 micron size. Because of the need to market a number of different grades it may be possible to selectively mine magnesite which has an adequately low iron content and in so doing of course a larger amount of magnesite with a high iron content will be obtained. Beneficiation, as discussed above, would purify each of the grades to an acceptable MgO content and then, additional to any chemically purified products, the grades which have naturally low iron could be selected as the premium natural grade.

Dr. Markovic emphasized that for a magnesite market it is not sufficient to produce a small or medium tonnage of very high purity MgO as grades down to 92% of MgO are also required and most buyers will take the lower grade along with a quantity of high grade. The box-work silicate structure which is evident in the Tasmanian Savage River magnesite after firing may be due to an advantageous impurity, i.e. calcium silicate, which can help in the sintering and recrystallization of the magnesite when it is dead-burned. In Basse Sambre experience, many buyers prefer material which is less pure in Cao and SiO_2 because it has better characteristics in brick-making. This does not necessarily apply to iron contamination however, and the material which the European suppliers are providing appears to be very good in this respect.

Dead Burning of High Purity Magnesite

In relation to chemically purified MgO, Dr. Markovic pointed out that very high purity MgO is more difficult to fire to dead-burned

condition that is slightly less pure material and that the MgO which the magnesium bicarbonate process will produce might prove very difficult to dead-burn to a dense state. Very high purity magnesium carbonate can require a firing temperature of 2000°C and may then give only a density of 3.0. Material which contains 1 or 2% of calcium silicates, FeO or calcium carbonate requires only 1800° and can give a density of 3.4. However, following other discussions, it seems possible to overcome the problem by briquetting procedures.

Heavy Media References

Dr. Markovic gave me a number of papers and patents, listed on page 31, describe the application of heavy media separation to coal in the size between 1 - 12 mm; the heavy media purification of magnesite; the use of wetting reagents which allow porous magnesites to be penetrated by water and heavy media in order to raise their density; and the methodology of heavy media analysis and its translation to expected plant performance.

VISIT TO DR. MITSCH, VEITSCHER MAGNESIT, VIENNA -
23 AUGUST, 1979

Physical Beneficiation, Marketing, Magnesite Assessment

Dr. Mitsch was my original contact with the Company and is their Chief Geologist. He is responsible for mine production and for the assessment of present deposits and possible new ones. Veitscher Magnesit produces about 250,000 tonnes/year of magnesium oxide in various forms, including that made from natural material from Turkey and has mines in the Styria region, Austria, where they mine for direct use following physical beneficiation. The actual mines are at Breitenau and at Trieben. At the latter mine they have been practising flotation of magnesite for about 20 years. It is at Breitenau that the hydrochloric acid pilot plant has been set up. The Veitsch mine is now closed because the magnesite is too high in iron. However, the brick-making plant is still located there.

Their research and development is done at Leoben where approximately 120 people are employed. Dr. Bouvier is Director of the laboratories, which are described and illustrated in a Company Brochure, p.32.

Dr. Mitsch provided specs on the best, or better grades, namely those suitable for BOF furnace bricks. He also quoted values for the standard ordinary good grade from natural material, usually Greek or Turkish for use in making bricks of slightly lower quality. This material, low in iron and aluminium, and relatively low in silica and lime is produced by physical beneficiation, including calcination steps. Flotation and heavy media separation are both used and they are applied selectively to materials of different, suitable, grades so as to minimize the amount of treatment necessary. The material which is floated usually comes from coarsely crystalline magnesite and flotation is carried out in order to lower silica and lime contents. The material is ground to less than 200 microns and standard flotation agents are used. Reputedly there is nothing special about the flotation sequence. The procedure is first to float silica and at the same time depress lime and magnesite and then to float lime, leaving magnesite behind. The reverse procedure is used in Gaps, Nevada where presumably lime is floated in the first stage.

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If applicable, heavy media separation is the cheapest and easiest, especially if material can be kept above 1mm at coarser ranges still. The lumps produced from such beneficiation can then be used in a rotary kiln for firing without briquetting, although it is always necessary to dry prior to this step. During preliminary roasting, chromite can be added when chrome magnesite compositions are required and this addition gives better sintering and densification during dead burning. For shaft kilns the lumps need to be greater than 20mm as compared with greater than 1-5mm for rotary kilns. Austrian practice is to use natural gas for firing and to use highest quality bricks in the highest temperature region of the furnaces and lower quality bricks in the forepart.

For high purity MgO it is absolutely necessary to avoid chrome in the later stages of the furnaces in order to avoid iron pick-up. The final firing temperature is 1800-1900^{o} depending on the starting material. As discussed elsewhere, the magnesite from the chemical plants must be briquetted subsequent to removal of hydroxyl at about 450-650^{o} and, following briquetting, can then be fired to full densification in one pass.

In this connection the extremely pure product from the hydrochloric acid pilot plant took approximately two years of effort to get the dead burning conditions correct. This included an intermediate firing, followed by hot or cold pressing. It now appears possible to get full firing in one pass.

With regard to the different crystallinities of material, some spar magnesite is mined in Austria by both Companies. A whitish porcelain-type comes from Turkey and Greece which can be floated and is then used direct. In European experience, silica and similar impurities increase towards the bottom of the deposits and silicified dolomites have just enough specific gravity difference from magnesite to be separated by heavy media processes. If this can be done it is a major beneficiation step and obviates many steps in later processing. In some cases a distinct colour differentates magnesite from the impurities, as in Greece where the magnesite contains serpentine as an impurity, this being black. Ore sorting of various kinds can thus be practised.

Assessment of World Magnesite Production

There is some world over-production but the future is not yet known. It is not likely that there will be a major increase in consumption. Even so, there is always a good possibility for first-class product which at present sells for $200-$250/tonne dead burned.

Also uncertain are the oil and gas prices in the future and therefore the energy cost for any process. The most effected will be sea-water and other high energy routes. This will certainly include the chemical processes which, however, are likely to be less affected than the seawater process.

On the world scene any new producers of purified magnesite will be those most affected by energy increases as the investment of the existing producers is already capitalized in the U.S.A. and the U.K. Both the American and the U.K. markets are self-contained; there is little or no import or export; the same applies to the Canadians. The Japanese have one or more seawater plants, so any production by Australia for sale to Japan would have to compete in economic terms with the seawater operation. However, the purity of the sea-water material is often not sufficiently high and boron contamination from the seawater process is often a problem. Anything above 100 ppm leads to attack on the bricks under severe operating conditions.

Assessment of the Development and Properties of Savage River Magnesite

There is need for a heavy media assay and for a float assay. Problems arise not primarily from silica content but from the lime content, especially in relation to solid solution with magnesite, i.e. tending towards dolomite. Also, as CSIRO is fully aware, there are big problems in separating iron from the magnesite because flotation does not remove chemically bound iron.

There should be a mineralogical and textural examination of the body of such cores as are available; in particular the boxwork dimensions should be examined to see whether the material is ameniable to heavy media separation. For this purpose the boxwork dimensions

should be of the order of several mm or greater. Boron content should be less than 100 ppm, with respect to the final magnesium oxide. It would be preferable therefore to analyse down to about 10 ppm in the starting material.

In Dr. Mitch's view, the decision whether or not to proceed with the Savage River development depends heavily on the results which are obtained with respect to physical beneficiability and chemical treatment. The mined grade is given by chemical analysis as, e.g. x-ray fluorescence but a detailed mineral grain study, heavy media studies, flotation etc. are vital to knowing how the material will purify, and these studies should be completed prior to any further drilling.

Should the results be promising, it will then be necessary to look for the best way to perform selective mining and blending. It is also vital to produce premium grade as a market leader and other grades will follow. Without such a market leader it will not be possible to sell the lower grade. Magnesium carbonate costs twice as much to ship as does does dead burned magnesium oxide, if not more, and also fetches a lower price. It is therefore necessary to process the material at least to the dead burned stage in Australia. In Austrian practice natural gas is the best, if available, and far easier to use even than heavy pure oil. If natural gas were available in Tasmania this would be the most suitable fuel. Alternatively it may be necessary to ship magnesite to Victoria.

Pilot and Full Scale Plants

For pilot plant testing a small shaft furnace would be suitable and Veitscher Magnesit have a small rotary kiln about 3-4m long for rotary kiln testing. Up to 10 tonnes/day seems to be a suitable pilot plant scale.

A viable plant would produce 40 tonnes/day in a dead burned condition from a shaft furnace or, say, 30,000 tonnes/year if a rotary furnace can be used. In fact, most new sea-water plants are approximately 60,000 tonnes/year.

VISIT TO VEITSCHER MAGNESIT RESEARCH LABORATORIES, LEOBEN - 10 SEPTEMBER, 1979

Magnesium Chloride Route

This visit was arranged by Dr. Mitsch. The persons concerned were Dr. Grill, who is the Chief Development Chemist, and Mr. Grohmann, who is on the plant and production side. These two have been responsible for the pilot plant which Veitscher Magnesit has constructed and operated for the thermal hydrolysis of magnesium chloride derived from magnesite ore. They make this chloride solution by dissolving magnesite, at least partially calcined, in 20% hydrochloric acid which is regenerated from the hydrolysis step. There are a number of steps, which they described in general outline, following the initial dissolution. A summary of the process is shown in Figure 1.

The HCl process starts with magnesite which is at least partially calcined in order to get rapid exothermic reaction with 20% HCl solution. Following dissolution the impure $MgCl_2$ solution is raised in pH by MgO (by-product) addition until Fe and Al hydroxides precipitate, which also brings down suspended silica and other materials. This step was apparently the most difficult to get right. The precipitate is filtered off and the filtrate treated with MgO and CO_2, or H_2SO_4, to precipitate $CaCO_3$ or $CaSO_4$. In the later stages of the operation I believe that they have switched to the use of sulphuric acid to precipitate gypsum. In either case the resultant calcium oxide content of the magnesium oxide product is about 1%. The Israeli material, where calcium is washed from the final magnesium hydroxide, has a lower calcium content but at a higher cost. This is due to the additional unit processes and also because the magnesium magnesium oxide is hydrated to a magnesium hydroxide slurry. This must be re-fired to remove hydroxyl water which represents an additional energy step.

Following calcium precipitation a second filtration removes solids to give the final $MgCl_2$ solution. Unit 6 in the flow diagram, Figure 1, is a thickener column which is in effect a spray dryer into which the magnesium chloride solution is introduced from the top, counter-current to the HCl and moisture-containing flue gases from the spray drying tower. The heat from these gases evaporates a considerable fraction of

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Figure 1. Magnesite-Hydrochloric Acid Route to MgO

1a. Feed, 100% 0.3 mm, partially or wholly calcined $MgCO_3$, or MgO dust + $MgCO_3$

1b. Same as 1a, but only sufficient to raise pH.

2. 20% HCl, regenerated.

3. Leaching tank.

4. Precipitation tank for iron, aluminium and undissolved residues (silica etc.)

5. Vacuum filter.

6. Precipitation tank for $CaSO_4$ or $CaCO_3$.

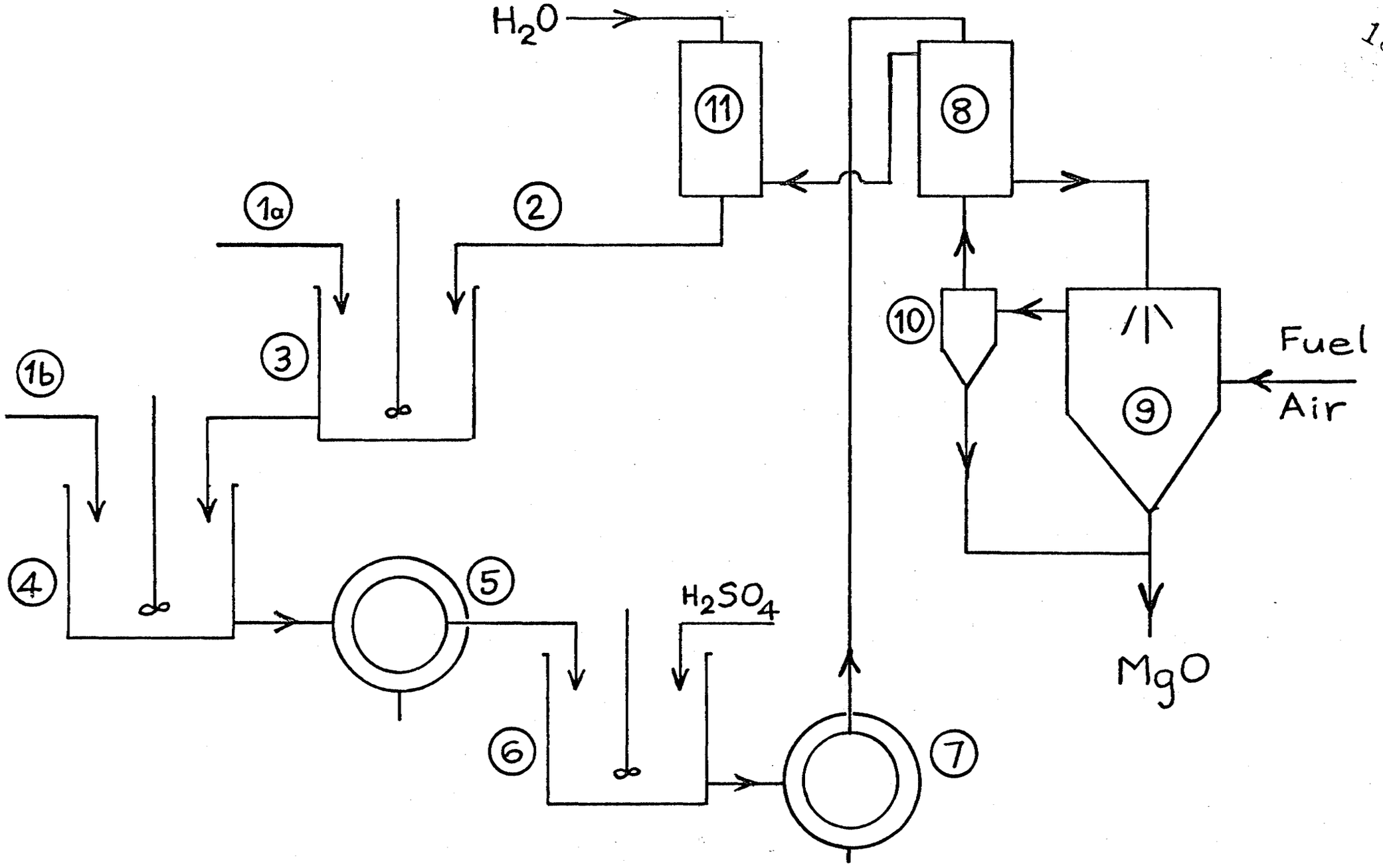
7. $MgCl_2$ solution vacuum filter.

8. Concentrator for $MgCl_2$ solution.

9. Spray roaster.

10. Cyclone for solids recovery.

11. Absorption tower for HCl vapour.



HYDROCHLORIC ACID PROCESS FOR MgO FROM MAGNESITE

the water from the solution. The exit gas stream, which consists of HCl and steam,is washed in a further column. This is packed,but could be fitted with internal baffles as an alternative. The output from the bottom of this final washing column, an "adiabatic packed column", is hydrochloric acid solution approximately 20%. This is returned to the first stage of the process for the dissolution of magnesium carbonate.

The spray roaster, for 10 tonnes/day, is about 7 m in diameter and about 3 times as high. These dimensions seem rather large for the weight produced but are presumably necessary to accommodate the very large expansion in volume which occurs when the solution is flashed to steam. Because of the formation of magnesium oxide by hydrolysis of sprayed droplets, the mean particle size is very small, namely 1 micron. The material is very light and feels like talc. It is also rather easily attacked by carbon dioxide and moisture from the air and, if stored for any period, must be protected. The spray nozzles are made of tantalum to resist corrosion and the plant has an automatic hydraulic system for lifting the sprays clear of the heating chamber should blockage occur. This is to conserve the nozzles and prevent them from overheating. The technology of this end of the process could be said to be well under control and Veitscher Magnesit staff thought that the main problems in getting the whole thing to go smoothly lay in prior steps. Although the chemistry is in principle simple, dissolving a carbonate in hydrochloric acid, precipitating iron, aluminium and silica at one pH, filtering, precipitating calcium carbonate or calcium sulphate at another, and obtaining the right reaction conditions and appropriate filterability of the solid products proved to be quite difficult to achieve and took a considerable amount of pilot and laboratory test work. Natural gas is used in the spray dryer as it is by far the cleanest fuel. It is also possible to use fuel oil although this is more expensive and less available locally. The use of coal is not very feasible because the ash content of the coal would contribute aluminium, silica and iron back to the magnesium oxide. This would be extremely difficult to overcome unless the coal was floated to a high degree of purity. The spray hydrolysis equipment, giving a reaction temperature of 600°C, is commercially available and was purchased by the Company from the firm of Ruthner in Vienna. The first stages of the process were, however, developed by Veitscher Magnesit themselves and put into pilot plant operation at approximately 10 tonnes/day. In this plant

they produced, towards the end of the test period, several thousand tonnes of extremely high grade magnesium oxide. The plant is at present in mothballs, or rather on a care and maintenance basis, until they decide whether it is economically feasible to build a full-scale plant. From the general composition of the Savage River magnesite, (>90% $MgCO_3$), they estimated that the process would work extremely well on that material. In the manufacture of high purity bricks from the magnesium chloride product it is necessary to compact the fine material in briquettes of the order of 20 mm in size. These are made in a Hargreaves press in much the same way as nickel pellets are made in the Western Mining Plant at Kwinana, W.A. After a preliminary firing, as I understand, in a rotary or shaft kiln they are gradually moved into temperature region where they are finally fired at about 1900°C to a dead-burned density of 3.3. Dead burned magnesite is subsequently crushed to about - 5 mm. for brickmaking and then bricks are made by the use of a suitable ceramic or pitch binder for very high purity material only ceramic binders are used. All the firing steps subsequent to production of the magnesium oxide from magnesium chloride solution also represent a significant energy cost.

In energy terms the cost of spray-drying, at 600°C, and probably prior calcination, are the major energy costs in producing the initial magnesium oxide. Less than 10% of the total energy requirements for the plant go into the dissolution and filtering steps. Depending on the grade of magnesium carbonate, the first dissolution step is exothermic and in any case the hot HCl gases and steam are driven from the spray drying towers to the first dissolution stage of the process still at quite a respectable temperature. Exothermic reaction is also obtained by calcining at least half of the magnesite prior to the acid dissolution step.

With respect to the magnesium bicarbonate process, which in some form or other has been around for a very long time, Dr. Grill thought that it was uneconomic compared with the seawater process and that it had only ever been used on about 5-10,000 tonne/year scale. Even then there were some impurity problems and the magnesium oxide product, which is regarded as a light magnesite oxide has, in general, been used only as a filler or packer rather than as a raw material for high density, high fired magnesium oxide bricks. Since deadburning has been successfully performed for the very fine product obtained after slaking

and dehydrating Israeli Amman process MgO, this problem need not be insuperable. However, the costs involved, or our estimates of them, should be compared with the sea-water plant costs and the cost for the magnesium chloride route.

Brickmaking

I also met with Dr. Bouvier who is a Member of the Board of the Company and in charge of the research laboratories. Most of the staff of approximately 120 people are concerned with brick formulation, testing of failed bricks, testing of raw materials and products for specifications and, to some extent, with the development of new processes. They are divided into six groups. These are: chemistry, mineralogy, process development, pilot plant testing, and one other, possibly services. This represents a considerable activity, which is mainly focussed on production methods, the specification of raw materials and of purified materials for suitability in brick manufacture, the specification of brick properties and the examination of bricks which have failed in a number of service uses in order to determine the causes of failure and means of overcoming it. Foremost among their tests are slag erosion tests which appear rather difficult to do on a small scale. They use a furnace about 900 mm in dia. and heated from electric arc. This gives a frozen slag at the wall, which protects the wall bricks, and the test bricks can be immersed in the central region. Views of their laboratories and test facilities are given in their Company brochure (see page 32). Overall, their effort in brickmaking technology would be hard to match without very considerable investment.

During a quick tour of the pilot area of the plant I was shown a number of different brick formulations, in the form of finished bricks, using both pitch and ceramic binders. However, no details were given and I presume this formulation stage is very much their Company's own technical knowhow. They mentioned that the Israeli's, who produce 50,000 tonnes of dead burned magnesium oxide per year, decided not to go into the brick manufacturing business after they had visited Veitscher Magnesit, because the technicalities and the art of brickmaking require substantial research, investment, and market acceptance, which is already available in the two Austrian companies. It may well be that the same applies to Australia, although Newbolds may have sufficient experience, and certainly have experience with high alumina bricks.

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Marketing

Dr. Bouvier had a number of things to say about the world market for magnesium oxide. At present it is somewhat over-supplied or capable of being over-supplied. However until 1974 there was a distinct shortage. In the last few years about five new seawater plants have been built, but several countries have in the meantime decided not to go ahead with seawater plants; these include Greece, Yugoslavia and Norway. The estimated economic production for an overall operation, that is to say including a plant which produces relatively high grade magnesium oxide by some chemical beneficiation process such as seawater or hydrochloric acid, is about 100,000 tonnes/year. Not all of the 100,000 tonnes need be of extremely high grade, as different grades are used in different parts of a blast furnace, open hearth furnaces, and rotary kilns. Nonetheless, it would be necessary to do a very careful market assessment before investing in such a large operation and to be sure that the raw material and particularly fuel costs were low enough to make the process competitive. Approximately $20/tonne for the raw magnesite at the input to a chemical process plant seems to be about a breakthrough price. This corresponds to a component of about $40-$50/tonne for the product magnesium oxide. In European energy price terms the hydrochloric acid process is marginally better than the seawater process, according to Dr. Bouvier and Mr. Grill. However, they may not have been in a position to disclose their exact figures, and certainly they have done a very large amount of economic costing on the various combinations of their process and various proportions of magnesium oxide produced by it. While Veitscher Magnesit have not, to date, licensed their process to any other producer, Dr. Bouvier indicated that there is a reasonable possibility that they would do so, presumably on some reciprocal basis such as joint venture, marketing the product, or getting some substantial royalty. They were not averse to discussing these ideas and Dr. Bouvier, as a Member of the Board, seemed receptive to further discussion should this be warranted.

Dr. Mitsch mentioned previously that Japan is at present more or less self-sufficient with seawater plants. Several people remarked, particularly Dr. Grill and Dr. Longin, that the purity of the seawater material is not quite good enough and that the better grades of natural magnesite can produce almost the same purity level at a very much lower cost. It would therefore seem important that if any process of a chemical nature is undertaken, it should produce material of the very highest

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purity, otherwise it will not compete on the world market and would not have the advantage of being a premium grade which would be the leading product allowing the remainder of the mined material also to be marketed.

VISIT TO GENERAL REFRACTORIES COMPANY, EUROPEAN GROUP, VIENNA - 11 SEPTEMBER, 1979

General Background to MgO Production and Use

Dr. Longin, the General Manager of the General Refractories Group, gave a rundown on the use of magnesite as a source for refractory bricks. Prior to BOF practice, the main use was in open hearth steel making furnaces and in blast furnaces. For these purposes a reasonably low iron content of the order of 1-2% in the initial material giving 2-4% in the product was sufficient. In Austria there were plentiful quantities of spar magnesite, namely material with very large crystals, of the order of 1 cm or more. This material has been mined since 1950 and beneficiated by flotation and heavy media. The Company has considerable experience in flotation as have Veitscher Magnesit. The General Refractories Group produces about 280,000 tonnes of magnesium oxide per year, about the same as their counterpart; some of this comes from Turkey, in the form of microcrystalline high purity natural material. About 60,000 tonnes comes from Kalkadiki in Greece, and 50,000 tonnes of "super grade"Amman product from the Israeli plant, in which European Refractories have a part share. The remainder comes from their own mines in Austria.

The early product, containing iron which formed magnesium ferrite, an extremely stable phase, was suitable in blast furnace operation and in open hearth steel making. However, with the introduction of basic oxygen furnaces, BOF, the requirement arose for a much purer product. This is because in the BOF furnaces oxygen reacts with the steel impurities to give carbon monoxide directly. This reduces ferric iron to iron metal and causes considerable shrinkage of the bricks as well as softening of the ceramic bond. Attack on the brick is then rapid and the bricks fail. While a considerable amount of relatively impure magnesite is still used for less demanding purposes, for basic oxygen furnaces in particular much higher purity must be obtained. Table 1 shows the purities for the bricks for this purpose, the product obtained from the Amman process in Israel and the usual grade obtained from the best natural material. Dead burned magnesium oxide made from the best natural material contains 0.25% of R_2O_3, i.e. a total of Fe_2O_3 and Al_2O_3. This is approximately the same as the product from seawater process. To obtain this level of impurity in natural grade material,

extensive flotation or heavy media separation is necessary. European Refractories, with two mines, one in Corinthia and the other in the Tyrol, with processing plants at each, initially began with heavy media in 1940. They used cone heavy media separation for larger material, cyclones for finer material. For the last twenty years they have also been using flotation, which they have substantially developed and adapted. The material from their mines is put to the various beneficiation processes, depending on the head grade as mined. From their deposit in Greece, which contains very low iron, they obtain high purity natural magnesite by the use of heavy media separation. The process is similar to that described by Dr. Markovic of Basse Sambre, originally invented by Professor Ignjatovic. It involves double burning for lime removal and the details of this have been discussed in a previous section. The Greek material contains olivine and serpentine as the primary host impurity. The magnesite itself varies in specific gravity from 2.2 to 3.0, depending on porosity, compared for example with 2.9 for olivine. The material after the initial burning and preconcentration is surface treated in the semi-caustic stage and then retreated in heavy media as previously described. The final product contains 97% MgO and a total of 0.25 of R_2O_3.

The 280,000 tonnes of sinter-grade magnesium oxide per year produced by the General Refractories Group is mainly in form of finished products. These are primarily bricks, but include gun and ramming compounds for furnace lining and jointing and for joining together of bricks. A small proportion is sold in the form of sinter to other companies. 95% of their production, as for Veitscher Magnesit, is exported to other parts of Europe. Their parent company in the U.S.A. produces 150,000 tonnes/year from seawater plants but this is consumed almost entirely within the U.S.A.

Dead Sea material from Israel is known as DSP, i.e. Dead Sea Periclase. The Company has a large investment in brick-making and a lot of its technology and market experience goes in using bricks appropriate to the market from the various sources of magnesite. This is the same as for Veitscher Magnesit.

Comparison of the Amann Process in Israel and that operated in the Pilot Plant of Veitscher Magnesit

In the Israeli plant the magnesium oxide produced contains unreacted calcium chloride. This latter is removed by washing, which gives an extremely low calcium content if required. However, this washing also causes slaking of the magnesium oxide, which must be then reheated in a multiple hearth furnace or rotary kiln to give "caustic" MgO which is then briquetted before final heating at 2000°C to give a dead burned product. In the Veitscher Magnesit product there is less than 1% calcium oxide, the bulk having already been removed by calcium sulphate or calcium carbonate precipitation. Consequently there is no need for a washing step. The material after briquetting, possibly after preliminary heating, is given a heat for consolidation and then a final heat in a shaft furnace, using natural gas, at approximately 1900° to give the dead burned product.

General Considerations Regarding World Supplies of Brick-Making Magnesium Oxide

(Dr. Longin)

Between the two Austrian companies, General Refractories and Veitscher Magnesit, the European market is essentially supplied. In addition, through their holding in the Israeli plant, the European Refractories Group can supply super purity MgO, approximately 50,000 tonnes/year. Veitscher Magnesit are considering whether or not to go ahead with a full-scale plant because they are not yet sure whether their product can all be sold. Because of a shortage in 1970/74 it appeared that supplies of dead burned high purity magnesium oxide would be sufficiently available. Therefore a number of countries contracted to install new seawater plants, five in all being constructed, each of approximately 60,000 tonnes capacity. This represents a very considerable European capacity.

Open hearth furnaces require approximately 12 Kg of magnesium oxide per tonne of steel, while BOF furnaces require only 2-3 Kg. Consequently, there has also been a decrease in demand, even though the amount of steel which is being made has been greatly increased.

The British market is internally supplied by Steetlys, and the American market is also internally supplied. This is also probably true of the Canadians. This means that outside of any possible domestic sales, markets for Australian dead burned magnesite would have to be found in Japan or Asia. The Japanese have a seawater plant, as have the South Koreans, and General Refractories has been asked to consider construction of a 100,000 tonne/year plant in China, where very large deposits of high purity natural material have been proved. Consequently any Australian company would need to produce a very high grade material which would have to be better than sea-water magnesite. Any steel-making company buying such material would almost automatically buy the lower grades which is required as well, but it would not buy the lower grades from a Company not supplying the top grade. It is therefore essential before any substantial work is done on further exploration of the deposit or on investment calculations costing any considerable amount of money, that a market in Japan, which seems to be the most likely customer, be assured. With the availability throughout the world of a very considerable capacity from Sea-water and, potentially, chemical plants, investment in a large plant in Australia would be risky in the absence of any definite market.

It is worth noting that although Ruthner are constructing the Yugoslavian plant and are prepared to offer it for sale elsewhere, the people at Veitscher Magnesit believe that the front end prior to the spray roasting stage is not as good as their's.

The conclusions with respect to markets were essentially the same as offered by Dr. Bouvier, the Director of the Veitscher Magnesit Research and Development Laboratories.

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EUROPEAN EXPERIENCE OF AUSTRALIAN MAGNESITE

Dr. Longin of the European Refractories Group has made a very large number of visits to Australia in connection with refractories and with the possibility of joint ventures with Australian companies. In particular, there is a magnesite deposit of good quality at Ravensthorpe which was owned by the Norseman Gold Mining Co. The European Refractories Group had made arrangements for a joint venture, with guaranteed production and marketing in the initial stages at least, with this Company. At this time (1977/8) Norseman was taken over by Hollandia and the European Refractories Group found that they were unable to reach agreement with the new management and the project lapsed.

Dr. Longin also referred to the dolomite material which BHP either owns or mines in South Australia.

Dr. Mitsch, Chief Geologist for the Veitscher Magnesit Company, has also visited Australia several times and has talked with Mr. Hudson and staff of Industrial and Mining Investigations Pty. Ltd. His particular interest in Australia at the present is the chromite deposits in the Lachlan region of N.S.W. These deposits have been looked at by a number of people including Division of Mineralogy, CSIRO, Perth. They appear to occur in rather small pockets, although of fairly high grade. It is possible that Veitscher Magnesit will enter into some mining agreement to work these deposits. This material is required for the manufacture of chrome-magnesite bricks which are part of the product range offered by the two Austrian companies.

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