582001

MCC 450

CSIRO

Institute of Earth Resources

Division of Mineral Chemistry

PRODUCTION OF MAGNESIA FROM SAVAGE RIVER MAGNESITE

PROGRESS REPORT NO. 9: JANUARY-SEPTEMBER 1982

J.H. Canterford and ... Rees

October 1982

Mineral Chemistry Communication

DISTRIBUTION

	Copy No.
Industrial and Mining Investigations Pty Ltd	
F. Beggs	1-7
CSIRO Division of Mineral Engineering	
A.F. Reid	8
CSIRO Division of Mineral Chemistry	
T. Biegler	9
J.H. Canterford	10,11
C. Moorrees	12
Records	13,14

This is copy _5_ of 14.

582002

CONTENTS

PRODUCTION OF MAGNESIA FROM SAVAGE RIVER MAGNESITE
PROGRESS REPORT NO. 9: JANUARY-SEPTEMBER 1982

SUMMARY

This report details the results of a number of laboratory-scale calcination and leach tests carried on out the first of a series of bulk samples of magnesite recovered from the Savage River deposit. The calcines have been characterized in terms of chemical composition, surface area and X-ray diffraction patterns. Leach tests using "standard" reaction conditions clearly demonstrate the influence of the calcination temperature and retention time on the rate and degree of magnesium dissolution. In general terms, the results are in agreement with previously reported data. The results, when combined with those obtained from additional bulk samples, should allow a reactivity index to be generated. This will be of significant benefit when engineering design and cost estimates are undertaken.

INTRODUCTION

The Division of Mineral Chemistry has undertaken a detailed examination of the calcination/carbon dioxide leach process for the production of high-purity magnesia from Savage River magnesite [1-12]. The major components of this study are listed below.
- Geology and mineralogy of the deposit.
- Chemical and mineralogical characterization of five "bulk" samples of crushed ore. These ranged from high-magnesite through to high-dolomite.
- Calcination behaviour of the five "bulk" samples - characterization of the calcines in terms of chemical and mineralogical composition, surface area, and leaching behaviour using standardized conditions. The effects of calcination temperature and retention time on the rate and extent of magnesium and iron dissolution, and on the [Fe×100/Mg] concentration ratio of the pregnant leach liquor were of prime concern.

- Detailed examination of the effects of slake time, slake temperature, carbon dioxide pressure, pulp density, leachant composition and agitation on the rate and extent of magnesium and iron dissolution, and on the [Fe×100/Mg] concentration ratio of the pregnant leach liquor.
- Determination of the cause of excessive iron dissolution.
- Development of a suitable method of removing iron from pregnant magnesium bicarbonate solutions. This involved characterization of the iron-containing precipitate and development of flowsheets for recovery and/or recycling of the aluminium sulphate used as the precipitant.
- Examination of conditions necessary for precipitation of the intermediate product and the calcination of the latter to magnesium oxide.
- Modification of the high-temperature, high-pressure pilot-scale autoclave leach rig to a form suitable for carbon dioxide leaching of crude magnesia calcines.
- Crushing, grinding and blending of a bulk sample of magnesite. Calcination in a technical-scale rotary kiln. Characterization (chemical, mineralogical and leaching) of the blended calcine.
- Batch leach tests using the pilot-scale rig. Verification of laboratory-scale results.
- Continuous leach tests (>24 h duration). These tests have not been completed.
- Preliminary capital and operating cost estimates. These were carried out by Wright Engineers using technical data provided by the Division of Mineral Chemistry.
- Technical discussions with IMI staff.

All of the experimental work has been carried out on diamond drill core (DDH MC1 and DDH MC2) and seventeen surface samples collected along Main Creek [12]. The latter have been used for mineralogical characterization purposes only, so that all work relating to processing has been carried out with milled diamond drill core.

Although the mineralogical studies [12] indicate that the major portion of the Savage River deposit is magnesite, calcination and leaching tests indicate that the behaviour of the feed is very much dependent upon the magnesite/dolomite ratio. It was concluded that, provided the dolomite content of the feed was less than 10%, then optimization should be based upon the behaviour of the magensite component of the feed. It

thus became clear that the logical extension of the laboratory- and technical-scale studies to the necessary pilot-plant study could only be undertaken if

(a) a more detailed exploration programme were carried out to ascertain more realistic estimates of ore reserves and grades, and to develop a suitable mining programme, and

(b) the extractive metallurgy of a range of bulk samples were known.

This information would allow a reactivity index to be developed. Part (a) can obviously only be carried out by IMI although Dr Malcolm Frost of this Division will be able to make a significant contribution. Part (a) will also result in the collection of suitable samples for Part (b). As yet, Part (a) has not been undertaken, partly because of the difficulties of the terrain. This has resulted in a delay in carrying out Part (b) as well as a significant slowing down of the commercial development of the Savage River magnesite deposit

To date, it has been possible to recover only one bulk sample for metallurgical testing. The results of this testwork are presented in this report.

EXPERIMENTAL

Approximately 70 kg of ore recovered from the bank of Main Creek was forwarded to the Division. The creek section was pegged at 25 m intervals over 175 m, each block being sampled at 1 m intervals. The sample can thus be considered to be reasonably representative of the surface exposure of the deposit along Main Creek. However, it cannot be regarded as representative of the whole orebody, or regarded as a typical feed. The ore was in lump form (-200 mm) and was coated with 1-3 mm of ferruginous clayey material. Much of the latter was removed by wet scrubbing before the sample was air-dried at ambient temperature for several days. The ore was then passed through a jaw crusher and a set of rolls so that the particle size was reduced to 100% -10 mm. The product was then mixed by repeated cone and quartering.

200 g grab samples were then calcined in an electrically heated muffle furnace for specified times at controlled temperatures. A sufficient number of the 200 g grab samples were calcined to give a minimum

- 3 -

of 1 kg of calcine formed at the given temperature for a given retention
time. Each calcine was then passed through a Braun mill to reduce the
particle size to 100% -150 μm. Each milled calcine was then homogenized
by rolling, and riffled samples for chemical analysis, surface area
determination, X-ray diffraction and leaching collected. The methods
used for this part of the study were the same as those used previously.
As with the standard condition leach tests carried out earlier in this
study, the tests are not designed to determine optimum leaching con-
ditions but are designed to illustrate the influence of calcination
conditions on leaching behaviour.

RESULTS AND DISCUSSION

Table 1 and Figs. 1-4 give the chemical composition and surface
areas of the calcines as a function of calcination temperature and
calcination time. The data indicate that this bulk sample contains
about 75% magnesite. It can be seen that the degree and rate of cal-
cination, as indicated by the MgO and CO_2 contents, increases as tem-
perature and retention time are increased. Maximum surface area and
thus maximum chemical reactivity is achieved at 700°C and a retention
time of 3 h. The results are consistent with previously reported data.

The X-ray diffraction patterns of the calcines were recorded
between $2\theta = 10°$ and $2\theta = 70°$. The relative intensities of the three
strongest reflections of magnesite and magnesia were accurately deter-
mined and shown to mirror the changes in magnesia content as a function
of calcination time and temperature.

The results of the leach tests are summarized in Table 2 and
Figs. 5-15. Only the magnesium data have been presented since the
amount of iron dissolved generally followed similar trends. Thus the
greatest amount of iron was dissolved from the most reactive calcines,
as determined by the rate and degree of magnesium dissolution. As
expected, the [Fe×100/Mg] concentration ratio of the leachates was
markedly dependent on calcination conditions, particularly temperature,
ranging from ~2 for the 700°C/3 h calcine to 0 for the 1000°/3 h
calcine.

The results are consistent with previously reported data and show that, to achieve maximum magnesium dissolution in the shortest practical retention time, calcination conditions must be carefully controlled. This particularly applies to the calcination temperature. As before, the trends in reactivity can be accounted for in terms of the degree of magnesite decomposition and the surface area of the calcine. As noted above, and as previously reported, the amount of iron dissolved is greatest with the most reactive calcine so that the iron concentration of the leachate prior to hydrated magnesium carbonate precipitation must be controlled by a combination of the leaching conditions and addition of aluminium sulphate.

PILOT-SCALE LEACH RIG

During the batch leaches carried out using the pilot-scale auto-clave rig, no significant materials handling problems were encountered [8]. However, the first continuous leach test of 24 h duration, the results of which have not as yet been formally reported, showed that further modifications to the rig were necessary. In the previous report [8] it was pointed out that the problems related to the instability of the pregnant leach slurry in the absence of a substantial carbon dioxide overpressure. The removal of the carbon dioxide atmosphere led to pre-cipitation of hydrated magnesium carbonate, which acted as a cementing agent. The end result was that the residue (mainly quartz) turned into a solid, immovable mass, blocking transfer lines, drainage valves, etc. These problems had not been encountered before in any hydrometallurgical processing carried out in the Division and necessitated substantial modifications to the rig in terms of valve design, minimizing the length of transfer lines, ensuring that transfer lines have a suitable angle to prevent solids build-up, etc. Valve design took a considerable amount of time and effort to ensure that there were no null points.

Figure 16 shows the design of the drain valve that has been manu-factured in the Divisional workshops and successfully tested on the pilot-scale autoclave rig. The valves have been fitted to autoclaves Nos. 1, 2 and 3 (from top downwards, Fig. 6, Ref. 7). The bottom autoclave, No. 4, is still fitted with a quick-action ball valve since

this autoclave is used only for holding purposes and is emptied every
10-15 min. During all tests carried out to date, no problems have been
encountered with the build-up of solids in the ball-valve stem.

STIRRED TANK TESTS

All of the leaching tests carried out to date have demonstrated the
importance of rapid transfer of carbon dioxide from the gaseous phase to
the liquid phase. In the liquid phase, some of the carbon dioxide will
be dissolved, but the majority will be in the form of minute bubbles.
To achieve the highest possible reaction rate, the bubbles must be dis-
persed evenly throughout the pulp, which must also be homogeneous, with
the bubbles having as high a surface area per unit volume as possible.
In other words, the bubbles must be as small as possible with the
highest possible bubble density. Bubble density and surface area are
affected by numerous factors including pulp density, gas pressure, rate
of agitation, gas injection technique, impeller design, baffling and
impeller position.

Whilst modifications were being made to the autoclave rig and the
laboratory-scale calcination and leach tests carried out, a significant
amount of time was spent carrying out stirred tank tests. The rig used,
shown in Fig. 17, consisted of a variable-speed drive shaft
(270-2800 rpm) with detachable impellers and a 25-litre capacity PVC
tank fitted with viewing ports. The tank had a dished bottom and its
dimensions, as well as those of the baffles, were similar to those of
the pilot-scale autoclaves. Solid as well as hollow stirrer shafts were
used; the latter were combined with Snyder impellers. All tests were
carried out with a constant volume of 5% solids slurry of crude Savage
River calcine; no frothing agent was added. For each of the following
impeller types, 45° four-blade turbine, six-blade straight turbine,
screw impeller and a six-blade back-slope turbine, the clearance between
the impeller and the bottom of the tank, and the stirring rate were
varied over wide ranges. The efficiency of stirring and gas-liquid
mixing was recorded photographically (all photographs were recorded at
1/500 s and fixed exposure conditions). The most efficient agitation
conditions were considered to be those that gave uniform mixing

vertically and horizontally and maximum bubble formation. These conditions were met with the four-blade 45° turbine Snyder impellers fitted in the pilot-scale autoclaves fixed approximately 10 mm above the bottom of the tank and rotated at 2800 rpm. Such a high rotation rate could not be used in the rig because of problems with heat removal from the shaft seals. The maximum rate of agitation in practice is about 500 rpm. At this rate, stirring/mixing efficiency is about 90%.

Figures 18-26 show the agitation/mixing achieved with a hollow shaft and a 110 mm four-blade screw impeller fixed 25 mm above the bottom of the tank. The increased agitation/mixing efficiency as the impeller speed is increased from 270 to 500 rpm to 2800 rpm is clearly observed. A major problem with this type of impeller is that it does not have an efficient lifting capacity so that even at 2800 rpmm mixing is not completely uniform over the full depth of the tank. Moreover, bubble size is fairly large, indicating only minimal shearing of gas bubbles produced at the submerged end of the hollow impeller shaft.

PATENT: MAGNESIUM OXIDE PRODUCTION

The Australian and International versions of the patent (PF 9574/81; PCT/AU82/00102) covering the production of high-purity magnesium oxide via calcination/carbon dioxide leaching, and iron removal by the addition of aluminium sulphate, have now been filed. An International Search has been carried out by the Australian Patent Office. All objections/examiner's comments have been satisfactorily answered. National examinations should be available in 6-8 months.

GENERAL COMMENTS

Apart from completion of the continuous pilot-scale leach tests, the next phase of the development of the Savage River deposit must involve further exploration to determine ore reserves and grades, and characterization of further bulk samples recovered from various regions of the deposit. It is essential that, if development is to proceed, discussions be held with IMI's consulting engineers as to process and

pilot-scale equipment design. There is no doubt that there will be many areas of experimental work that will need to be carried out to assist with design work. For example, it will be necessary to measure or to estimate settling rates, filtration rates, etc. Because the Division does not have the expertise to carry out the design work, it will be necessary to receive advice as to what data are required.

ACKNOWLEDGEMENTS

REFERENCES

1. J.H. Canterford and P.T. Everson, Production of magnesia from Savage River magnesite, CSIRO Division of Mineral Chemistry Report IRR 1028 (1979).

2. J.H. Canterford and P.T. Everson, Production of magnesia from Savage River magnesite, CSIRO Division of Mineral Chemistry Report IRR 1053 (1979).

3. J.H. Canterford and P.T. Everson, Production of magnesia from Savage River magnesite, CSIRO Division of Mineral Chemistry Report IRR 1074 (1979).

4. J.H. Canterford and C. Moorrees, Production of magnesia from Savage River magnesite, CSIRO Division of Mineral Chemistry Report IRR 1106 (1980).

5. J.H. Canterford and C. Moorrees, Production of magnesia from Savage River magnesite, CSIRO Division of Mineral Chemistry Report MCC 260 (1980).

6. J.H. Canterford and C. Moorrees, Production of magnesia from Savage River magnesite, CSIRO Division of Mineral Chemistry Report MCC 267 (1980).

7. J.H. Canterford and C. Moorrees, Production of magnesia from Savage River magnesite, CSIRO Division of Mineral Chemistry Report MCC 302 (1981).

8. J.H. Canterford and C. Moorrees, Production of magnesia from Savage River magnesite, CSIRO Division of Mineral Chemistry Report MCC 391 (1982).

9. J.H. Canterford, P.T. Everson and F.J. Moyle, Magnesia from magnesite by calcination/carbon dioxide leaching: influence of calcination conditions, Proc. Australas. Inst. Min. Metall., No. 277, 45-52 (1981).

10. J.H. Canterford and A.F. Reid, Magnesium oxide production, Australian Patent Application PF 9574/81; International Patent Application PCT/AU82/00102.

11. A.F. Reid, Production of refractory grade MgO from magnesite - European experience, CSIRO Division of Mineral Chemistry Report MCC 207 (1979).

12. M.T. Frost, The Savage River magnesite deposit, CSIRO Division of Mineral Chemistry Report MCC 351 (1981).

Table 1. Chemical composition and surface area as a function of calcination conditions.

| Calcination conditions | | Surface area | Composition (%) | | | | |
Temperature (°C)	Time (h)	(m^2/g)	MgO	CaO	Fe_2O_3	CO_2	Balance[*]
600	1	27.77	44.41	2.77	3.25	48.00	1.57
600	3	35.61	50.61	3.39	3.50	40.67	1.83
600	5	54.57	60.92	4.07	4.07	29.31	1.63
600	18	59.19	74.10	4.52	5.02	14.98	2.18
700	1	45.62	49.31	4.60	3.18	38.11	4.80
700	3	95.43	73.16	5.33	3.31	12.90	5.30
700	5	59.47	76.91	6.80	4.88	5.94	5.47
700	18	44.79	79.64	7.13	4.68	2.75	5.80
800	1	89.18	64.57	4.78	2.92	22.28	5.45
800	3	24.90	80.08	6.87	3.64	1.14	8.27
800	5	16.27	79.81	6.77	3.74	0.73	8.95
900	1	53.29	70.47	6.79	3.35	9.20	10.19
900	3	2.94	78.09	7.47	3.70	0.37	10.37
900	5	1.55	79.23	8.31	4.37	0.84	7.25
1000	1	4.97	79.46	8.46	4.36	0.37	7.35
1000	3	0.70	79.53	8.13	4.49	0.30	7.55

[*]Insoluble in 1:1 hydrochloric acid.

Table 2 Autoclave leach test data.[*]

Test number	1	2	3	4	5	6	7	8
Calcination time (h)	1	1	1	1	1	3	3	3
Calcination temperature (°C)	600	700	800	900	1000	600	700	800
Calcine Mg content (%)	26.8	29.7	38.9	42.5	47.9	30.5	44.1	48.3
				Magnesium concentration (gpl)				
Leach time (h)								
0.08	0.42	2.80	5.99	3.90	0.24	2.34	8.51	2.98
0.25	0.91	3.16	7.49	4.71	0.64	2.72	10.81	5.24
0.50	1.06	3.25	8.50	6.20	1.00	2.99	11.84	8.31
0.75	1.07	3.26	8.72	7.32	1.56	3.06	12.00	9.88
1.00	1.08	3.27	8.73	8.07	2.01	3.07	12.01	10.82
1.25	1.08	3.27	8.74	8.26	2.46	3.08	12.01	11.35
1.50	1.10	3.27	8.74	8.50	2.81	3.09	12.00	11.56
1.75	1.09	3.28	8.75	8.61	3.36	3.09	12.00	11.66
2.00	1.09	3.27	8.74	8.69	3.77	3.09	12.00	11.67
Mg extraction (%)[†]	13.6	36.7	74.9	68.2	26.2	33.8	90.7	80.5

Table 2 continued.

Test number	9	10	11	12	13	14	15	16
Calcination time (h)	3	3	5	5	5	5	18	18
Calcination temperature (°C)	900	1000	600	700	800	900	600	700
Calcine Mg content (%)	47.1	48.0	36.7	46.4	48.1	47.8	44.7	48.0

	Magnesium concentration (gpl)							
Leach time (h)								
0.08	0.34	0.11	5.40	6.82	1.77	0.11	8.19	4.20
0.25	0.64	0.16	5.91	9.44	2.85	0.34	9.66	6.69
0.50	1.07	0.30	6.34	11.61	4.60	0.61	10.90	9.95
0.75	1.44	0.48	6.39	12.17	5.95	0.86	11.37	11.55
1.00	1.87	0.55	6.40	12.26	7.06	1.12	11.48	12.30
1.25	2.29	0.65	6.41	12.30	7.73	1.37	11.49	12.41
1.50	2.59	0.81	6.40	12.31	8.24	1.66	11.50	12.41
1.75	2.88	0.96	6.40	12.31	8.56	1.91	11.49	12.40
2.00	3.05	1.12	6.40	12.31	8.71	2.16	11.49	12.41
Mg extraction (%)[†]	21.6	7.8	58.1	88.4	60.4	15.1	85.7	86.2

[*]3% solids, 0.5 h slake, 15.5°C, 1200 rpm, 100 psig CO_2.

[†]At 2 h leach time.
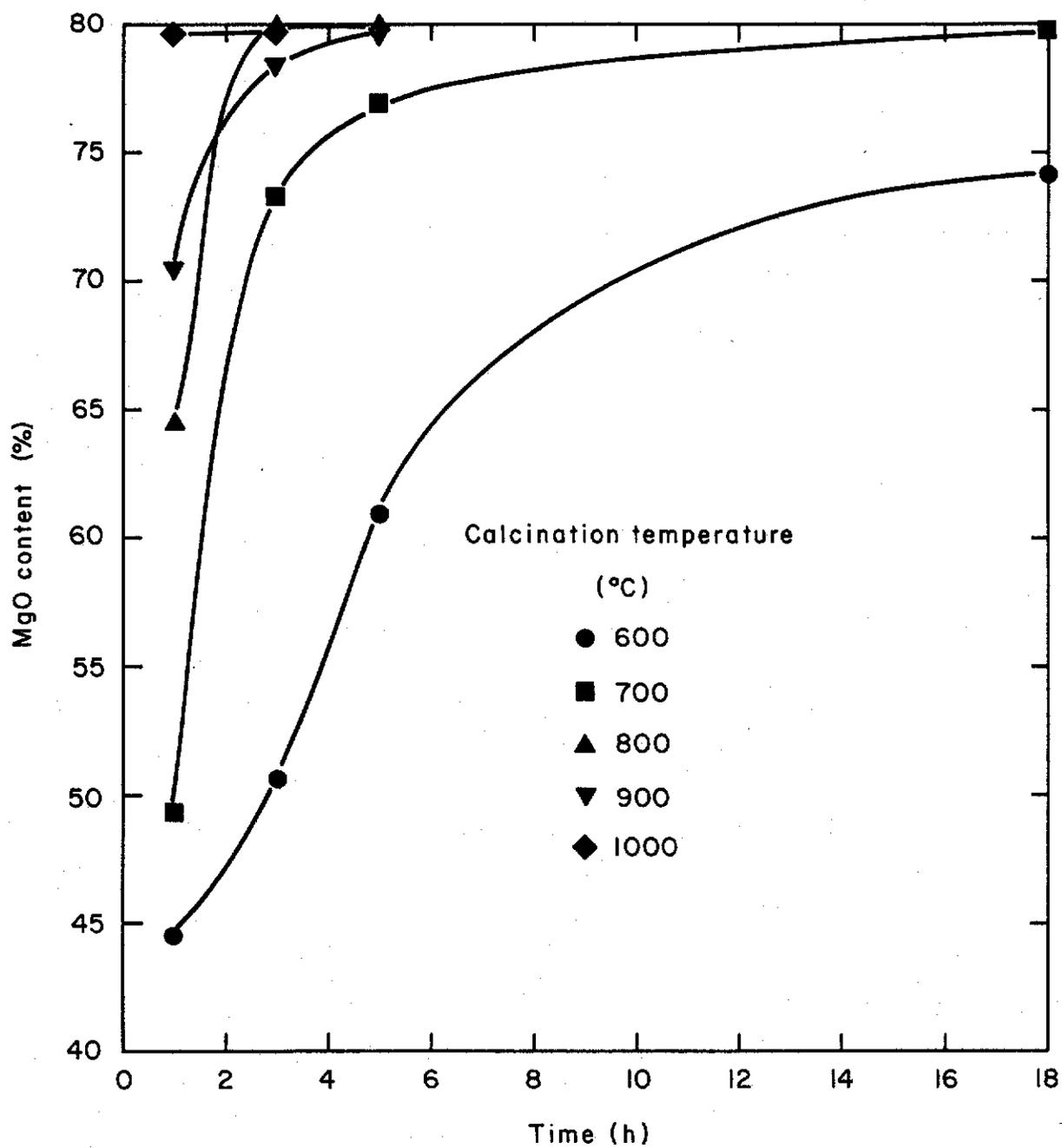
Fig. 1. MgO content of calcine as a function of calcination time.
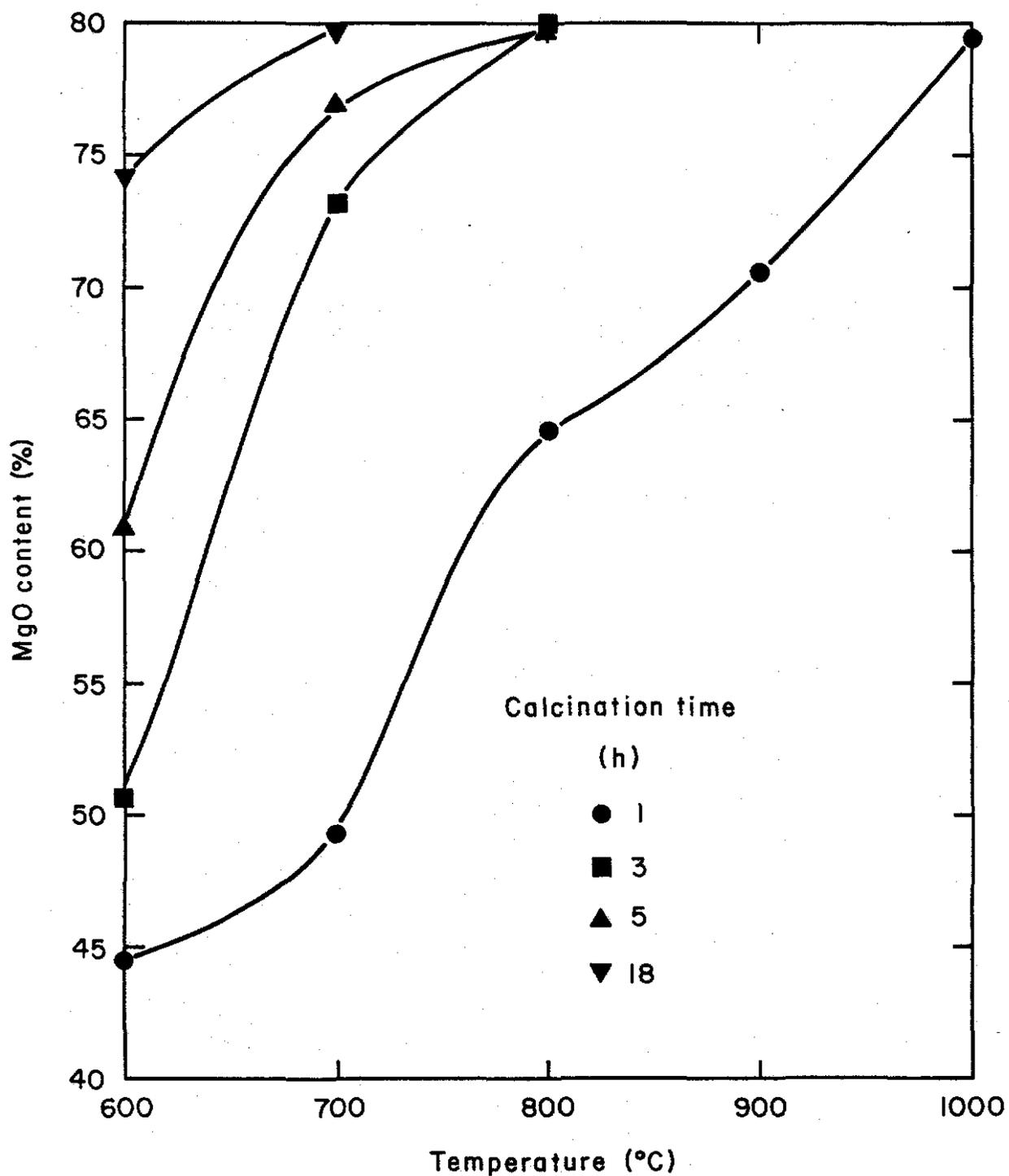
Fig. 2. MgO content of calcine as a function of calcination
temperature.
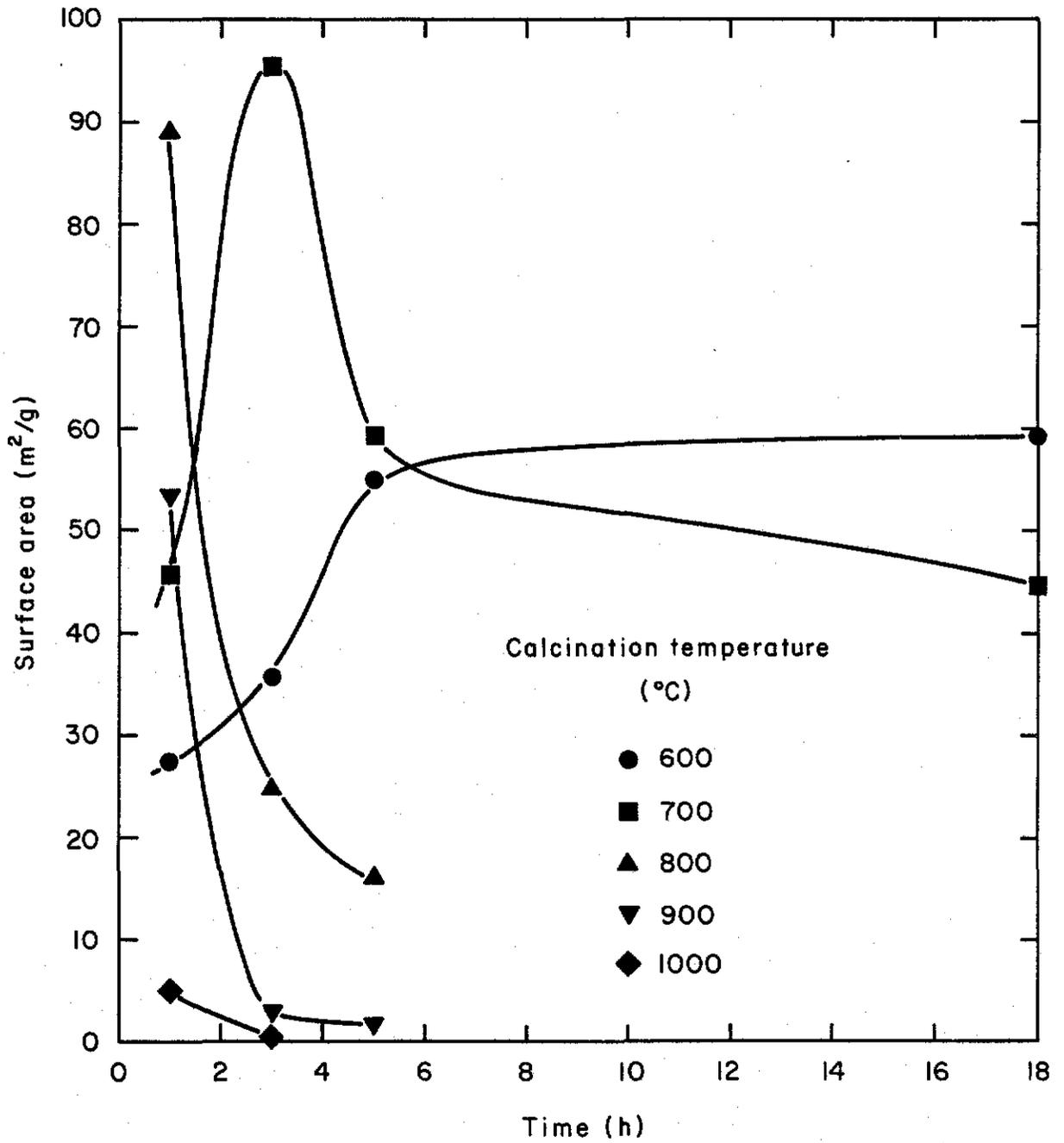
Fig. 3.   Surface area of calcine as a function of calcination time.
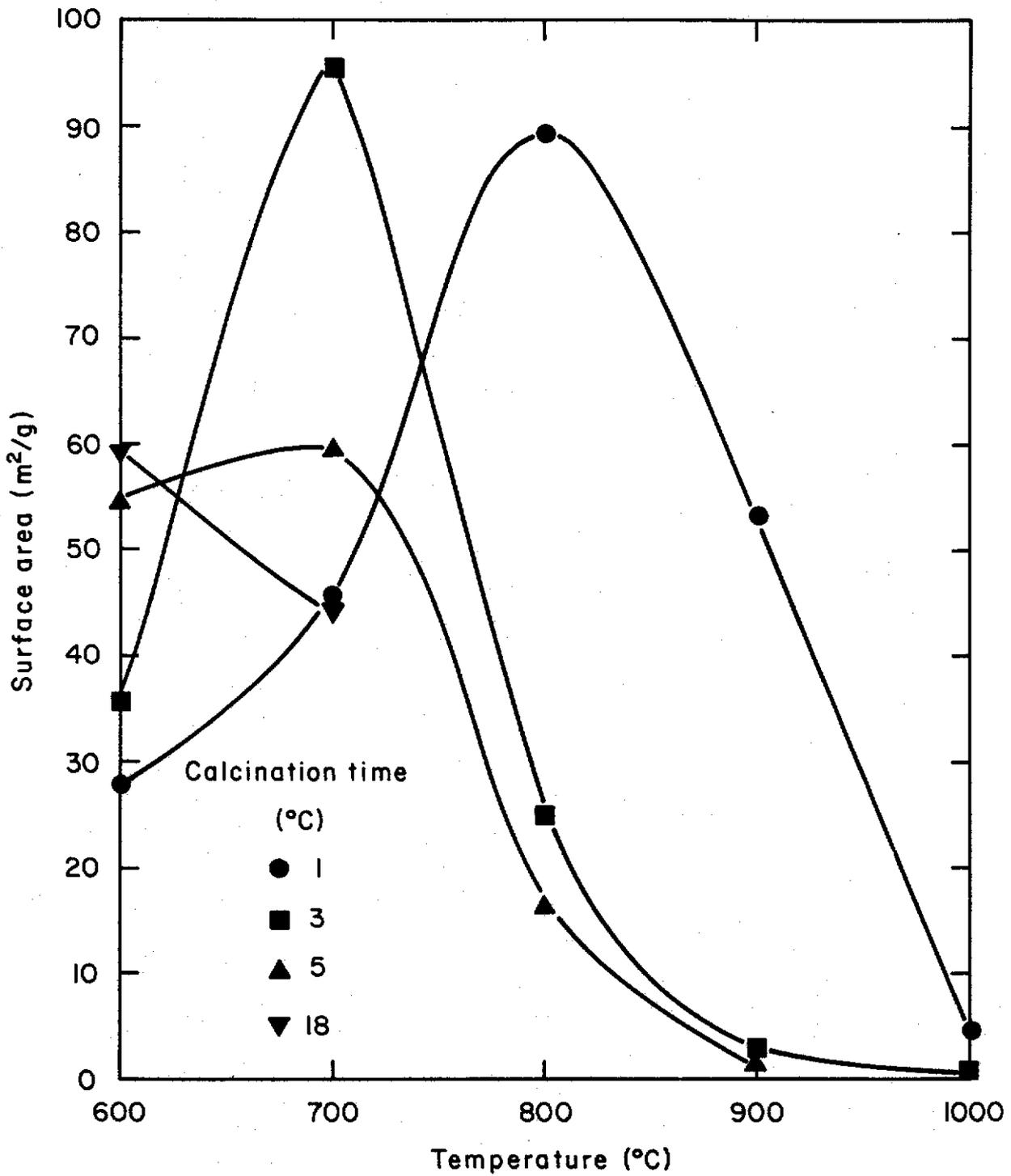
Fig. 4. Surface area of calcine as a function of calcination
temperature.
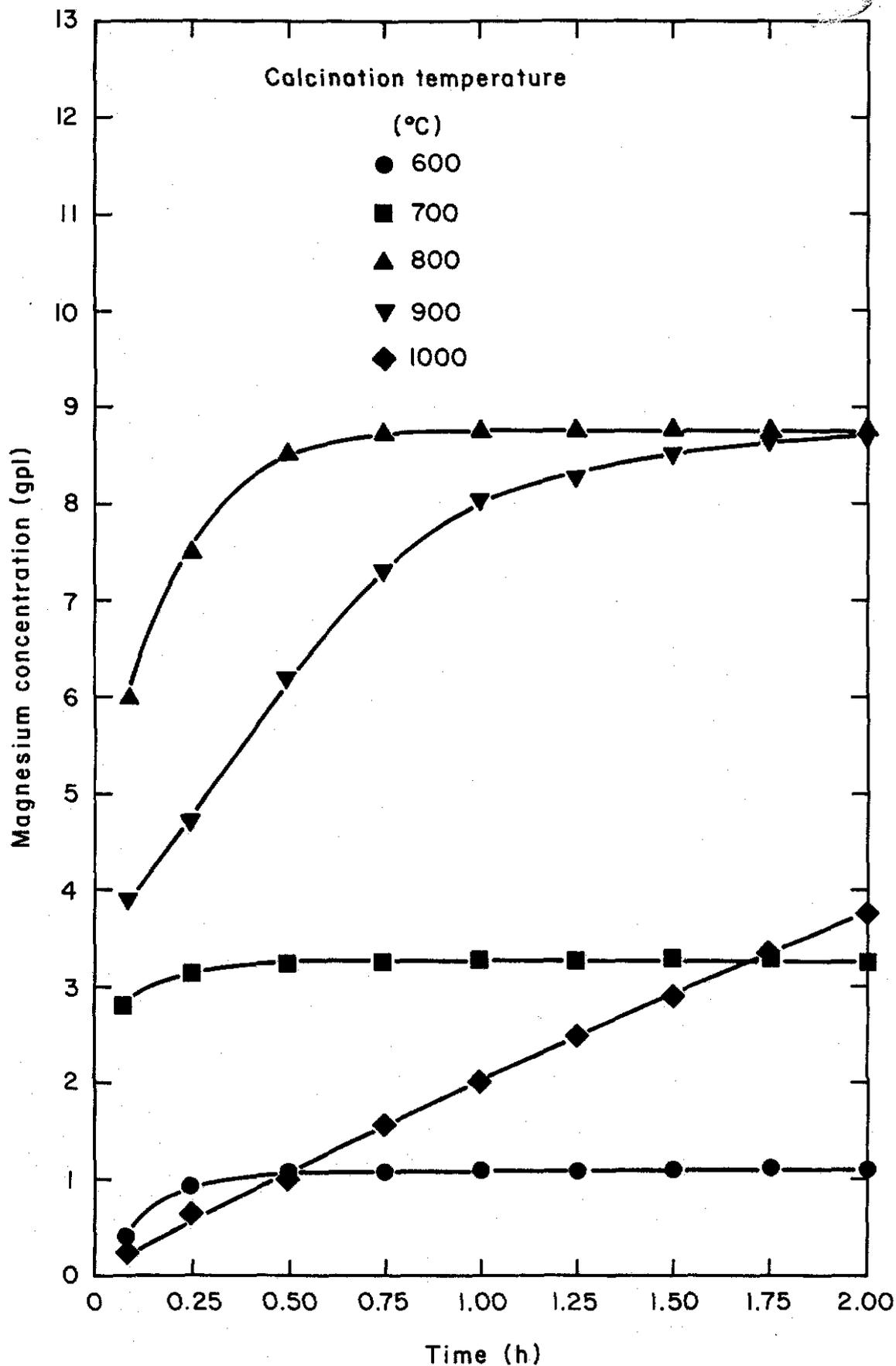
Fig. 5. Autoclave leach test data – magnesium concentration as a function of leaching time: calcination for 1 h at various temperatures.
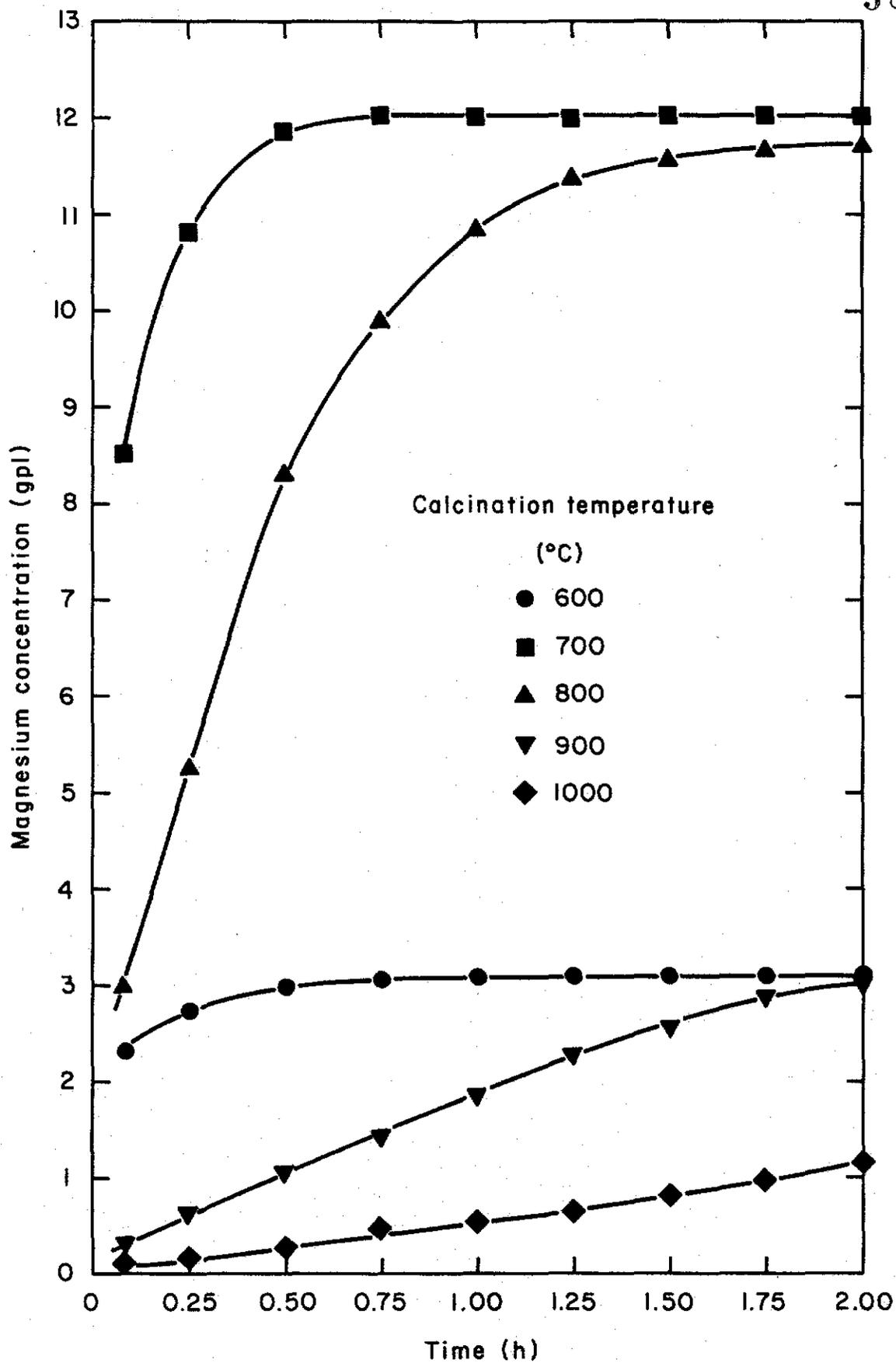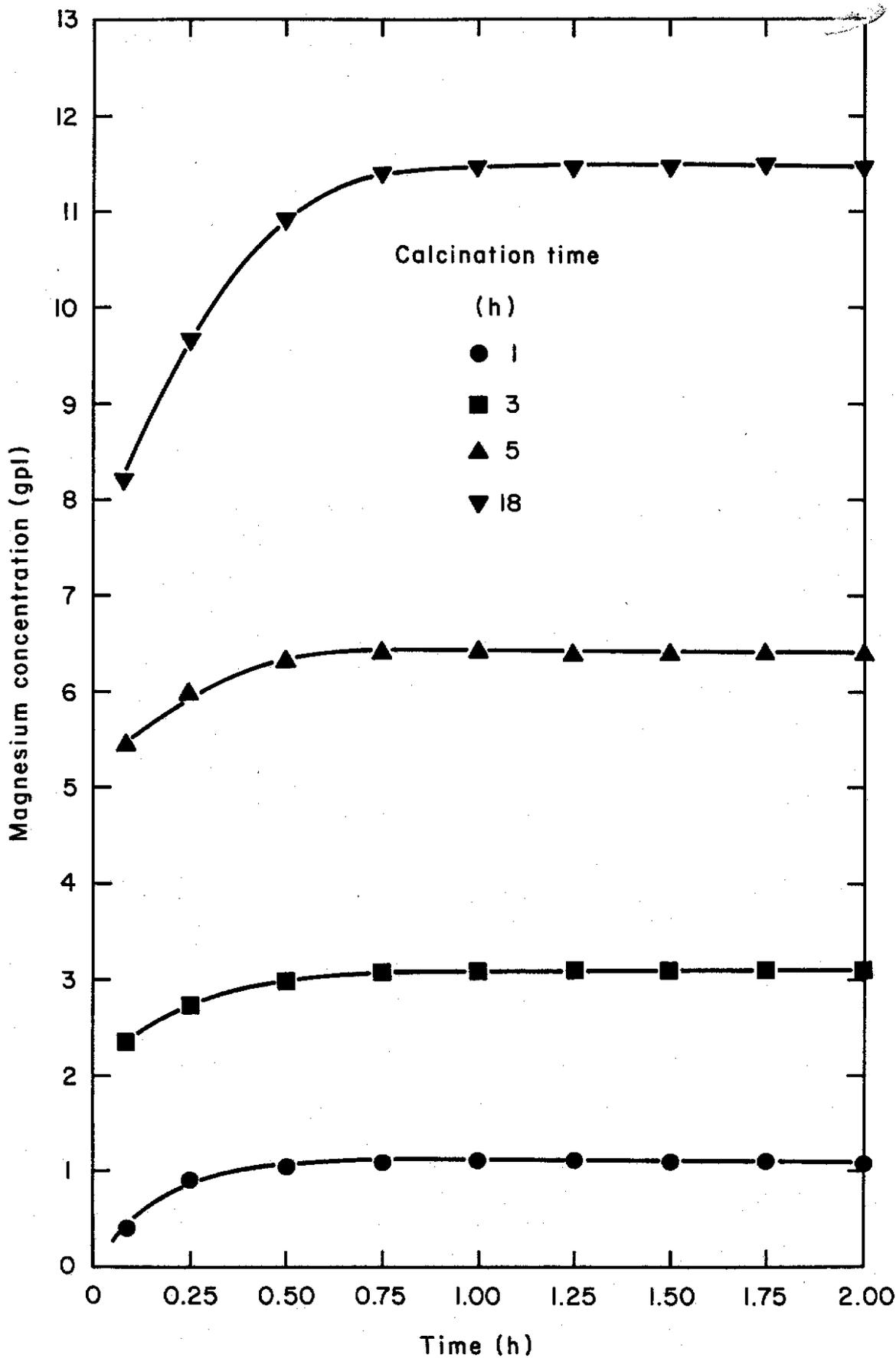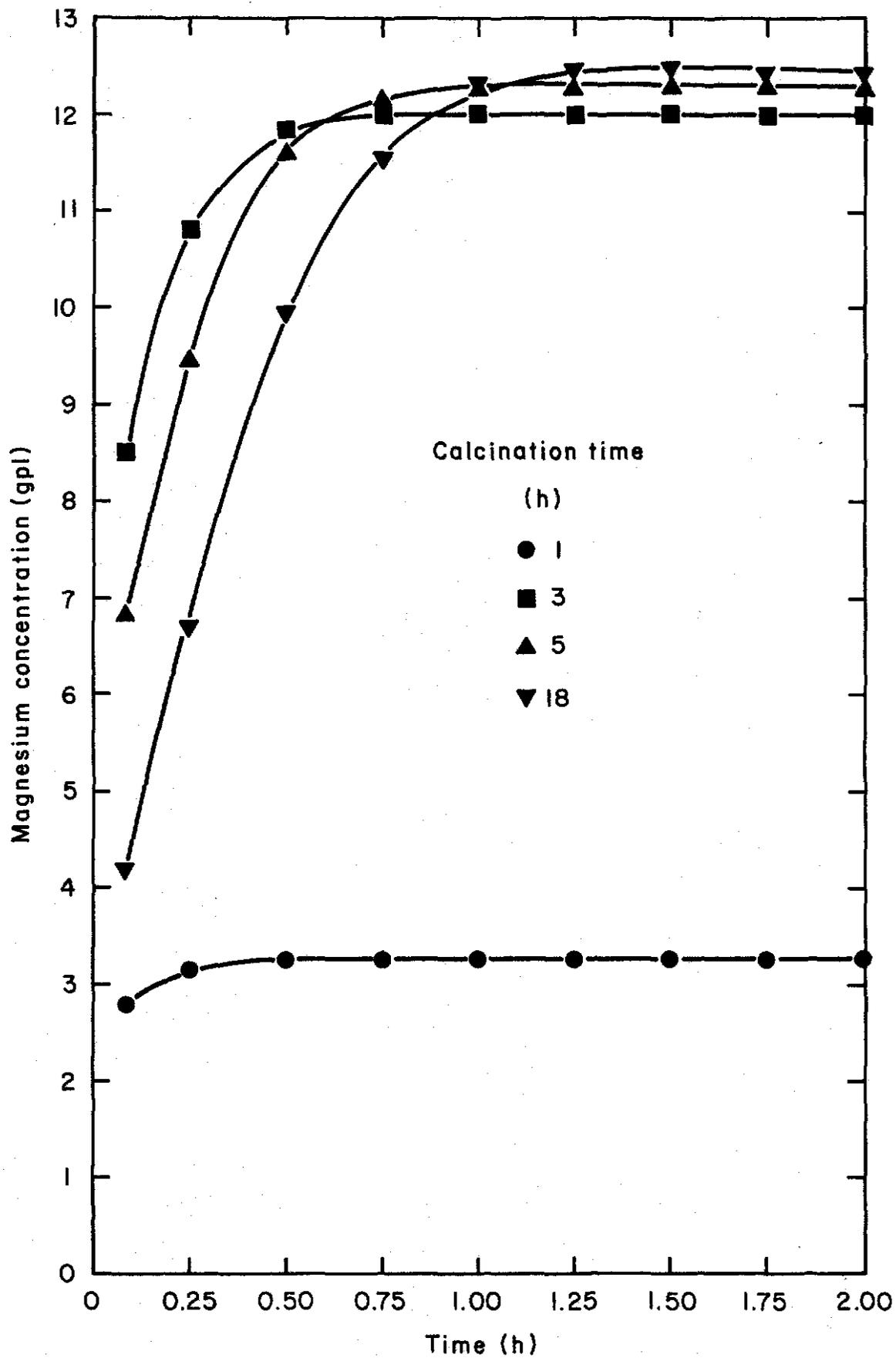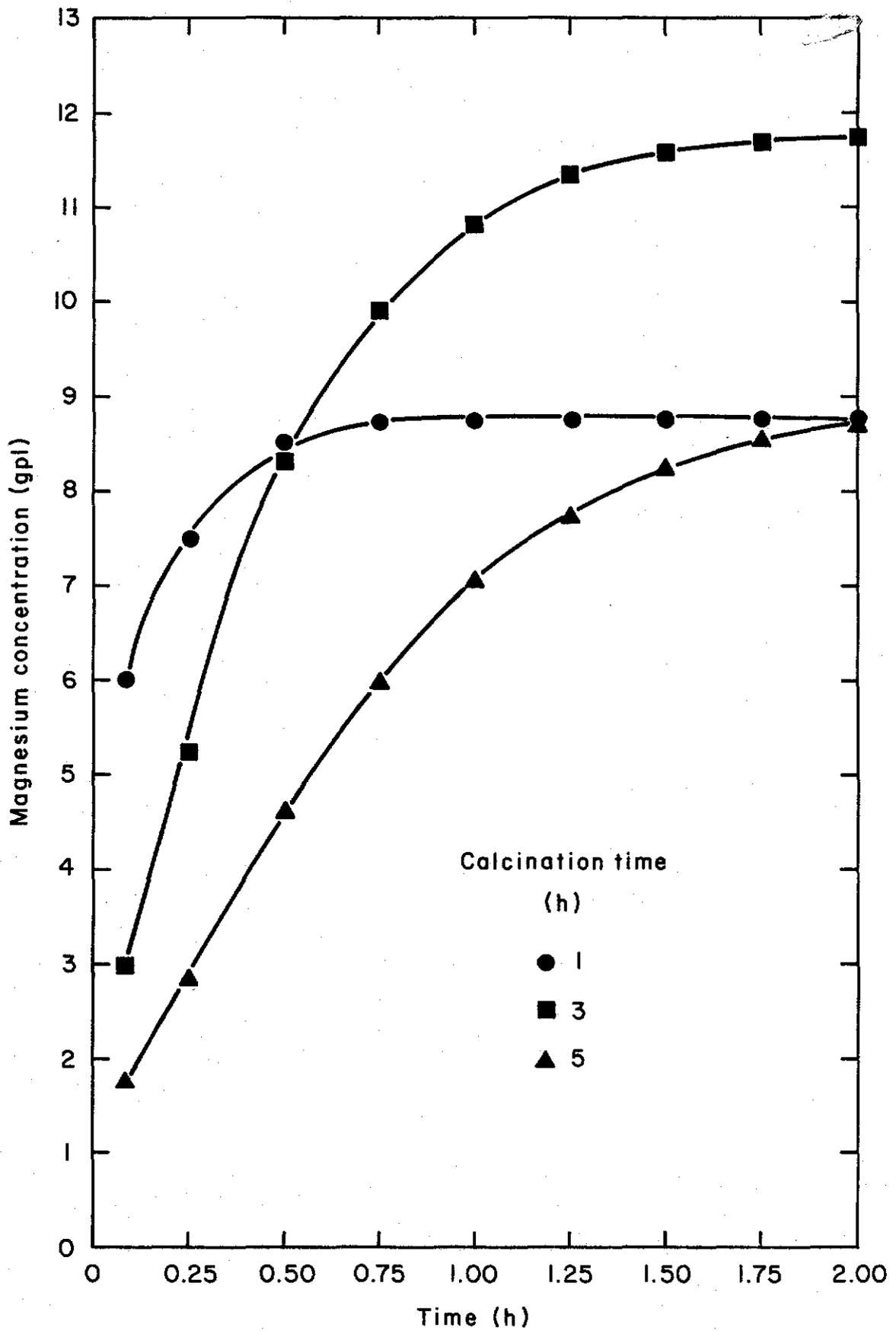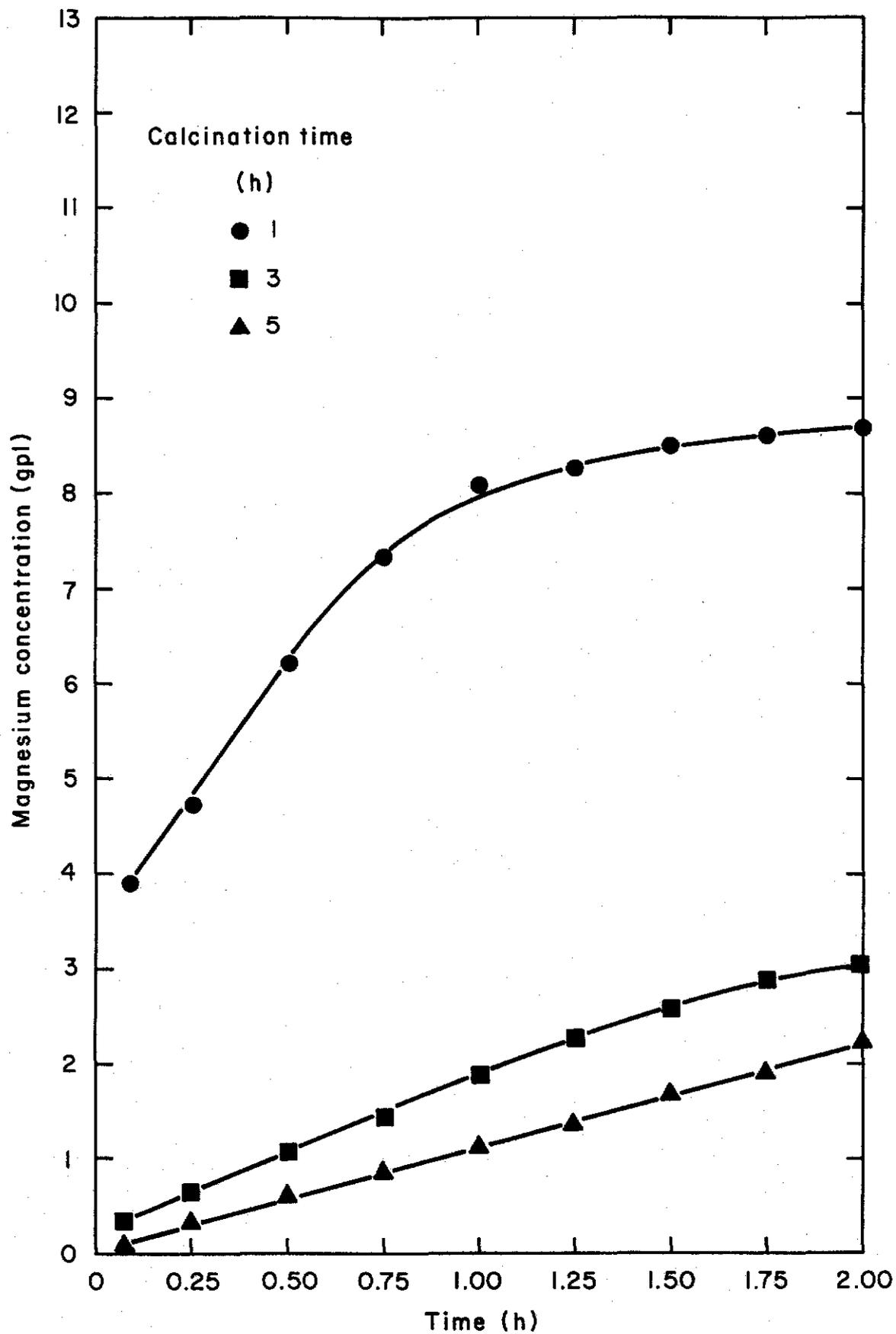
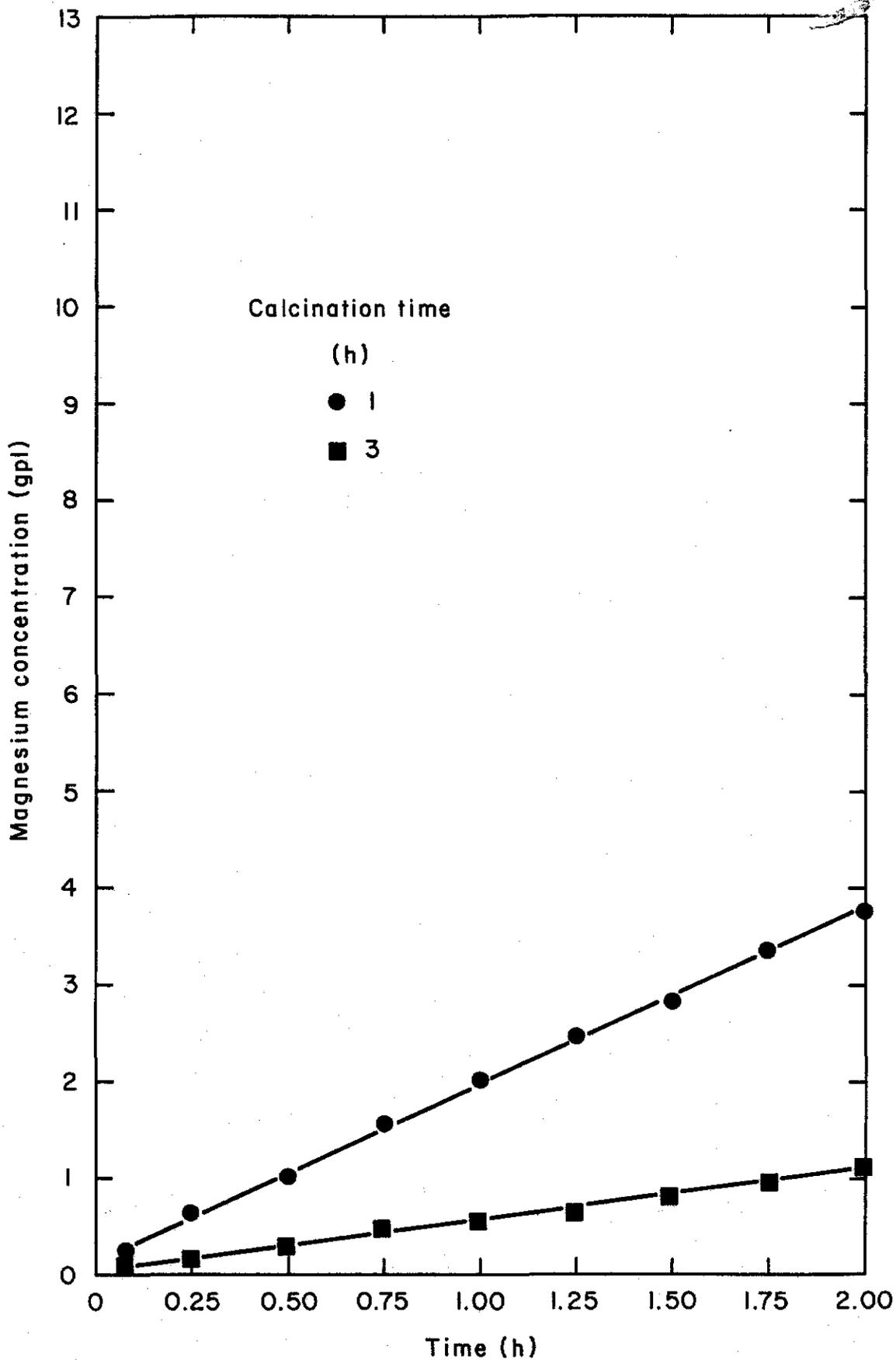Fig. 6. Autoclave leach test data — magnesium concentration as a function of leaching time: calcination for 3 h at various temperatures.
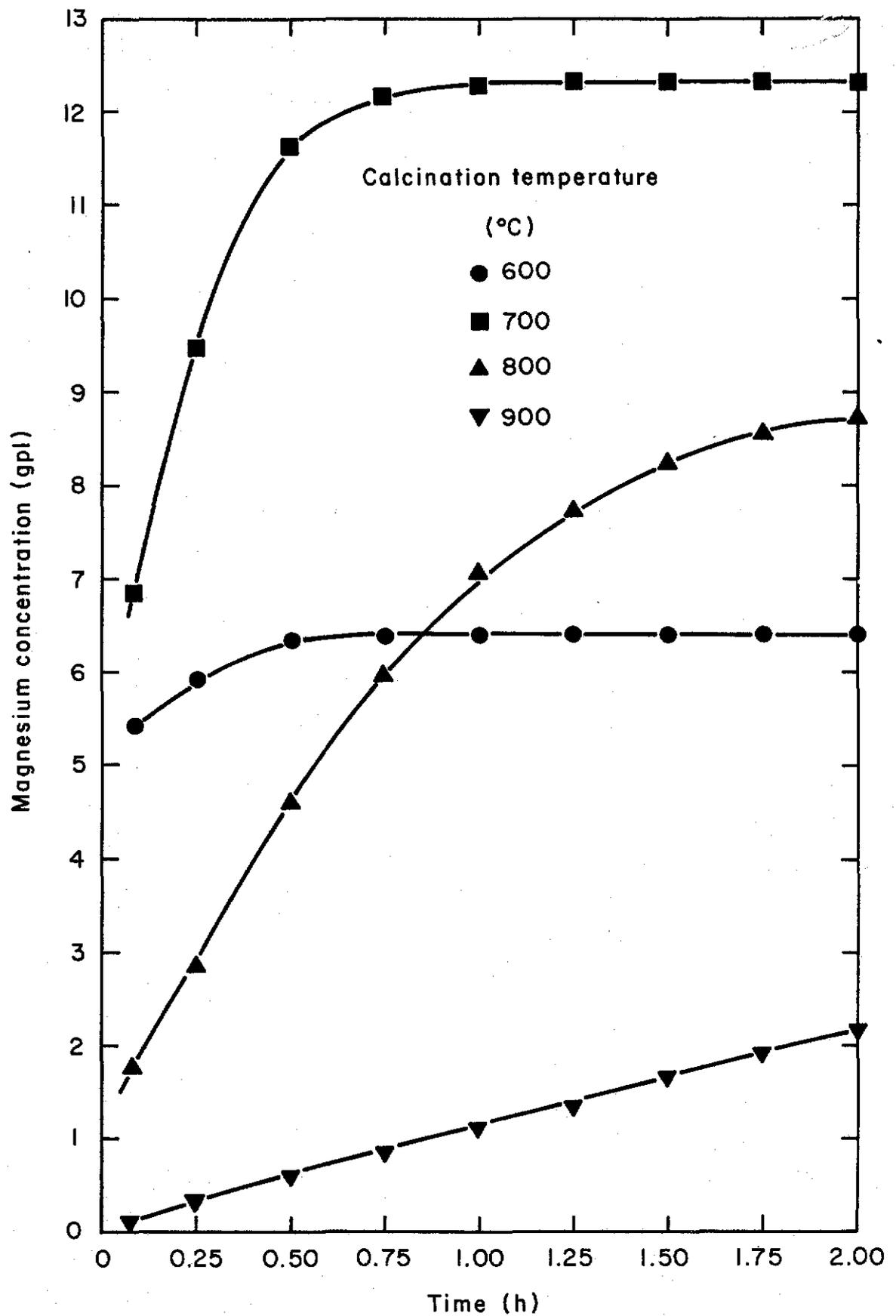
Fig. 7. Autoclave leach test data – magnesium concentration as a function of leaching time: calcination for 5 h at various temperatures.
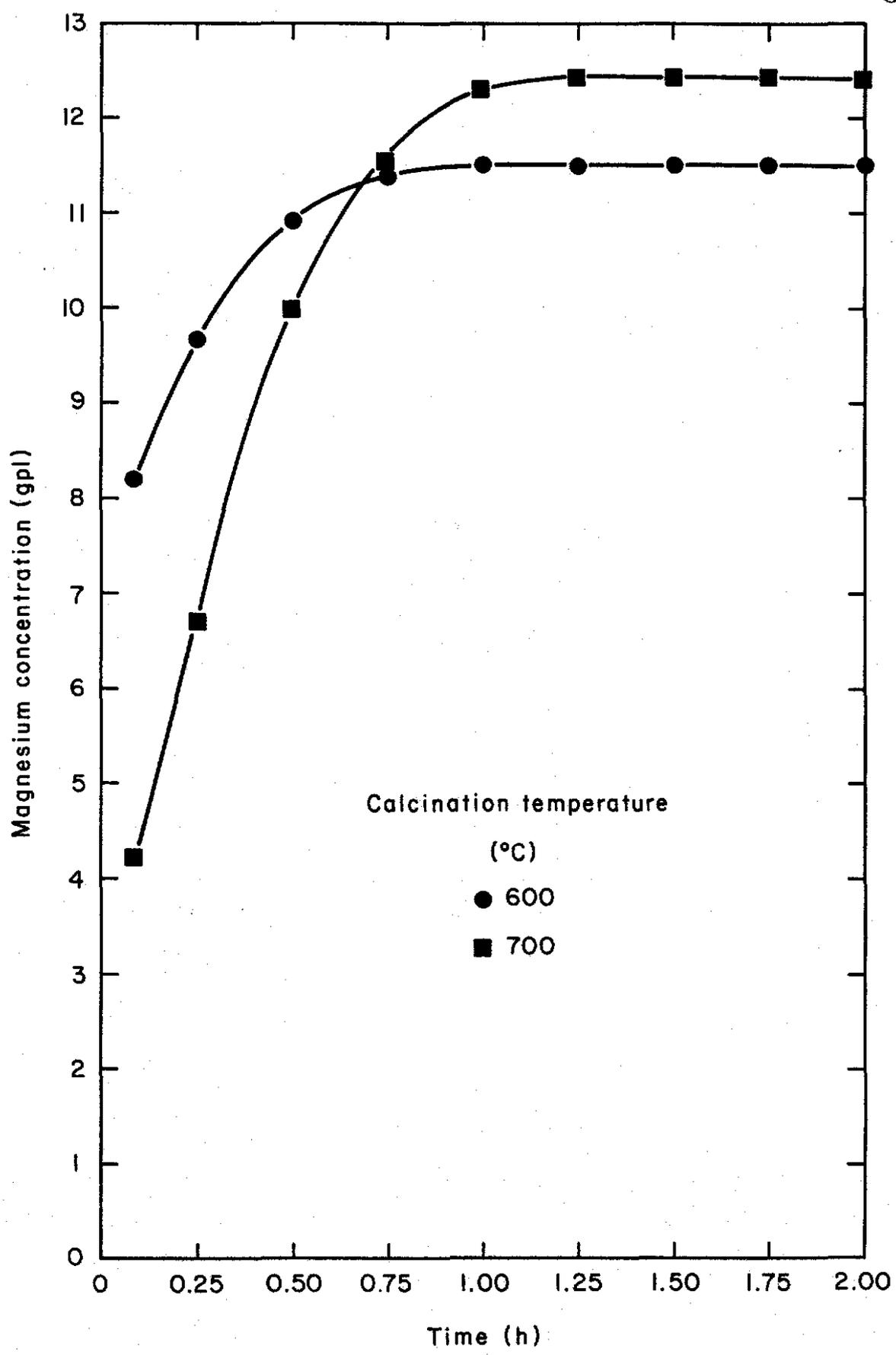
Fig. 8. Autoclave leach test data – magnesium concentration as a function of leaching time: calcination for 18 h at various temperatures.

Fig. 9. Autoclave leach test data - magnesium concentration as a function of leaching time: calcination at 600°C for various times.

Fig. 10. Autoclave leach test data – magnesium concentration as a function of leaching time: calcination at 700°C for various times.

Fig. 11.   Autoclave leach test data – magnesium concentration as a
function of leaching time: calcination at 800°C for various
times.

Fig. 12. Autoclave leach test data — magnesium concentration as a function of leaching time: calcination at 900°C for various times.

Fig. 13. Autoclave leach test data – magnesium concentration as a function of leaching time: calcination at 1000°C for various times.
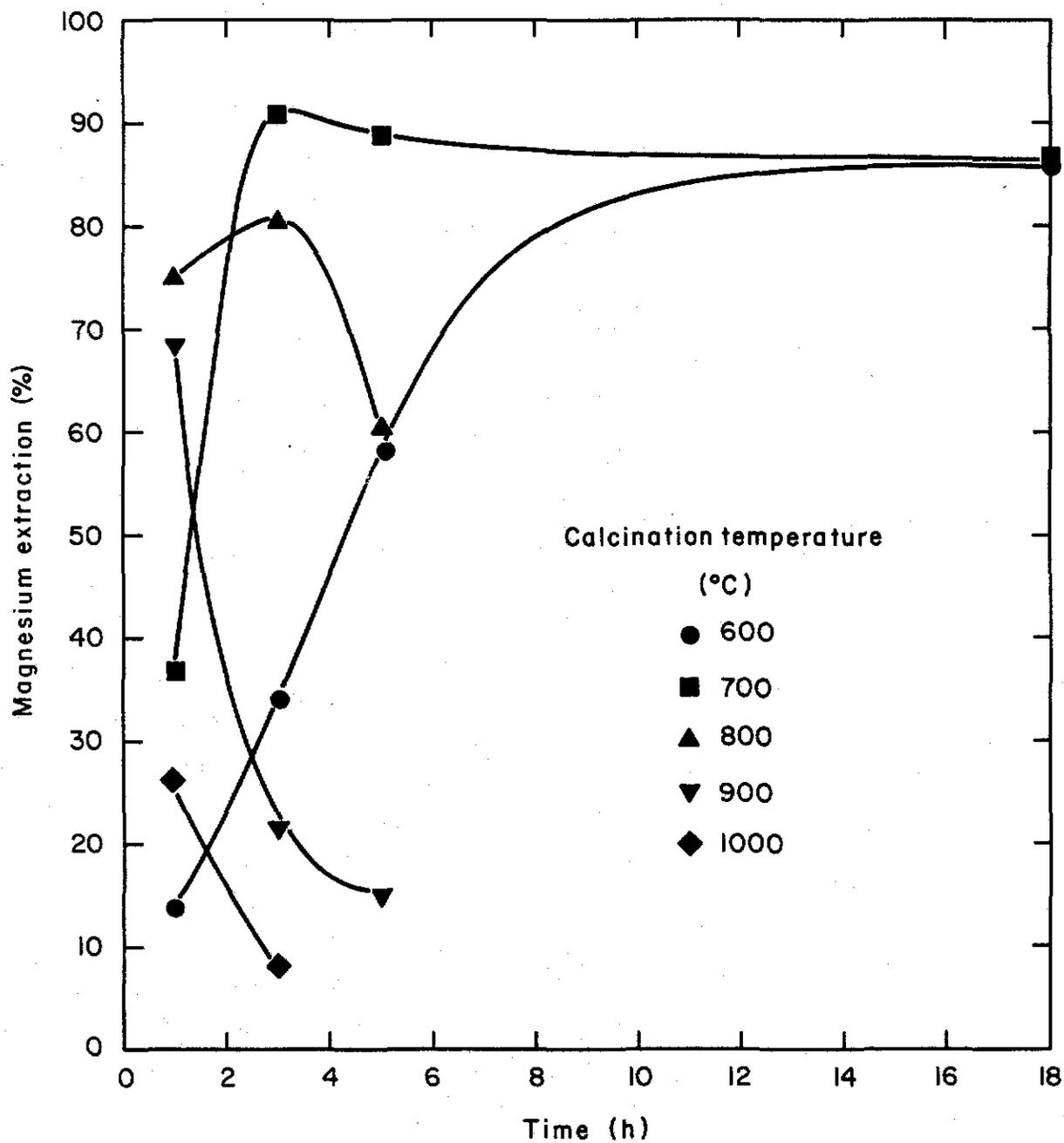
Fig. 14. Magnesium extraction as a function of calcination time for various calcination temperatures.
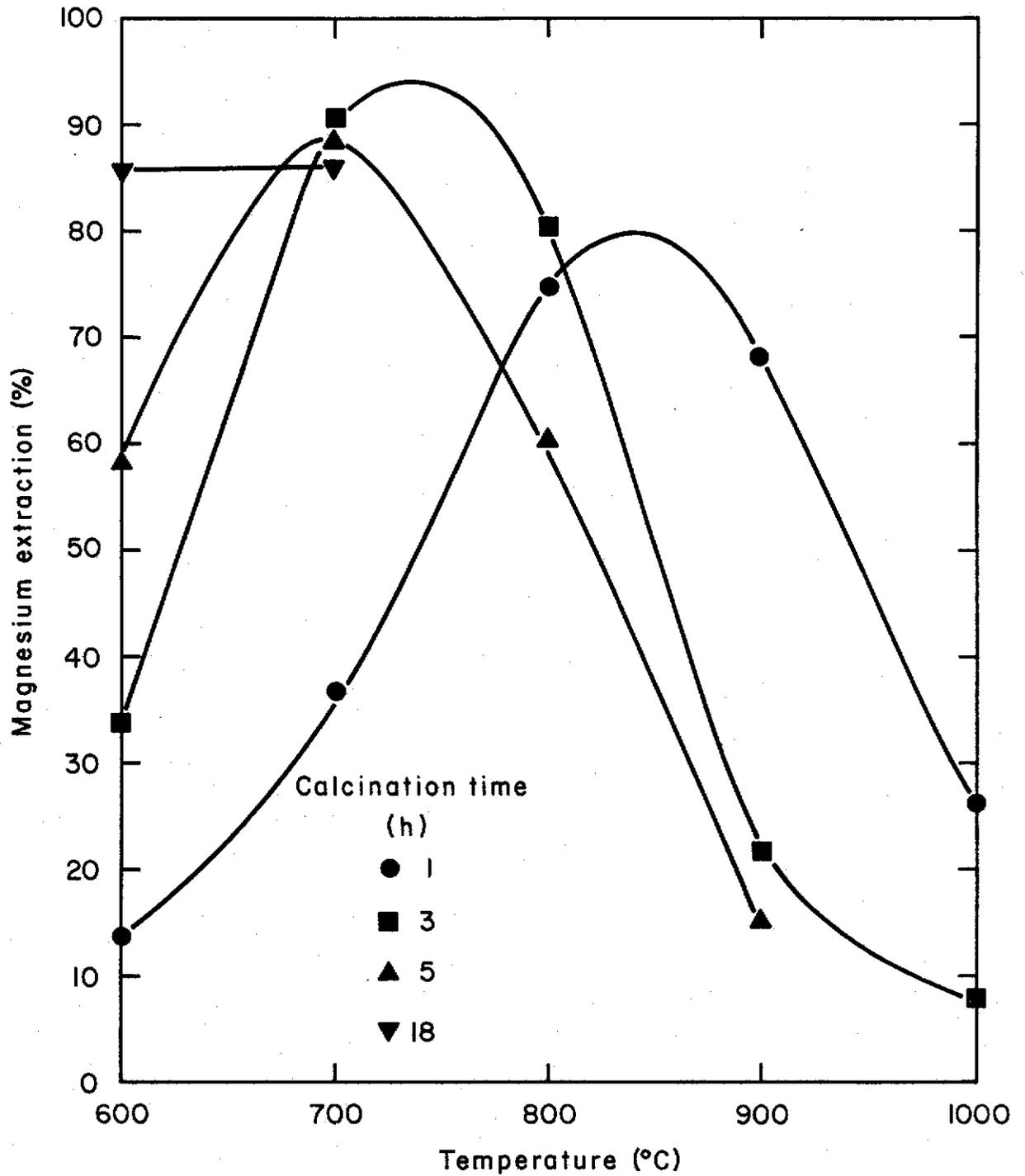
Fig. 15. Magnesium extraction as a function of calcination temperature for various calcination times.
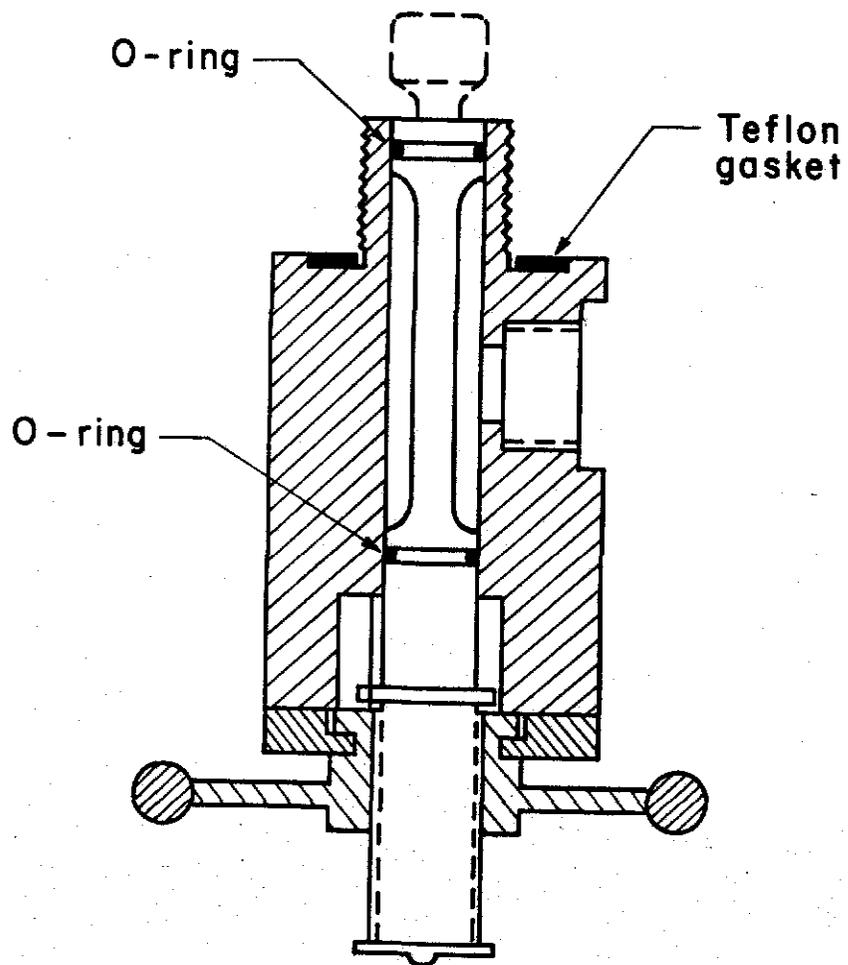
Fig. 16. Drain valve for pilot-scale autoclave leach rig.
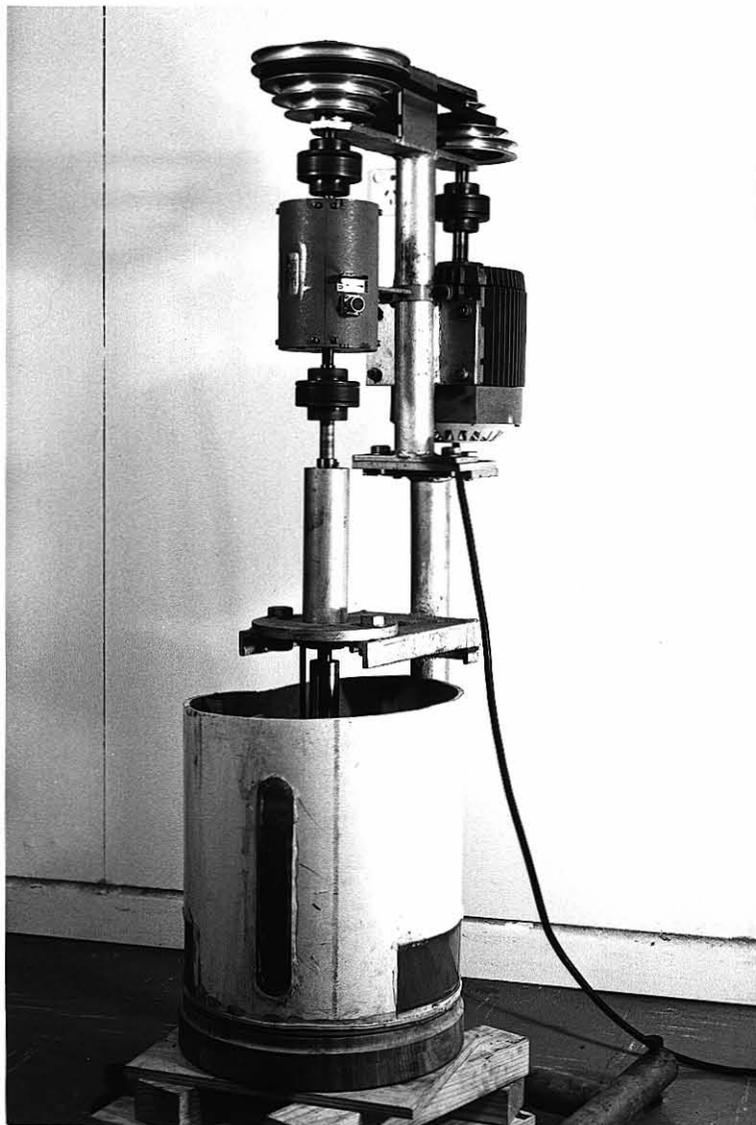
Fig. 17. Stirred tank equipment.

Fig. 18. Horizontal mixing: 270 rpm.

Fig. 19. Horizontal mixing: 500 rpm.
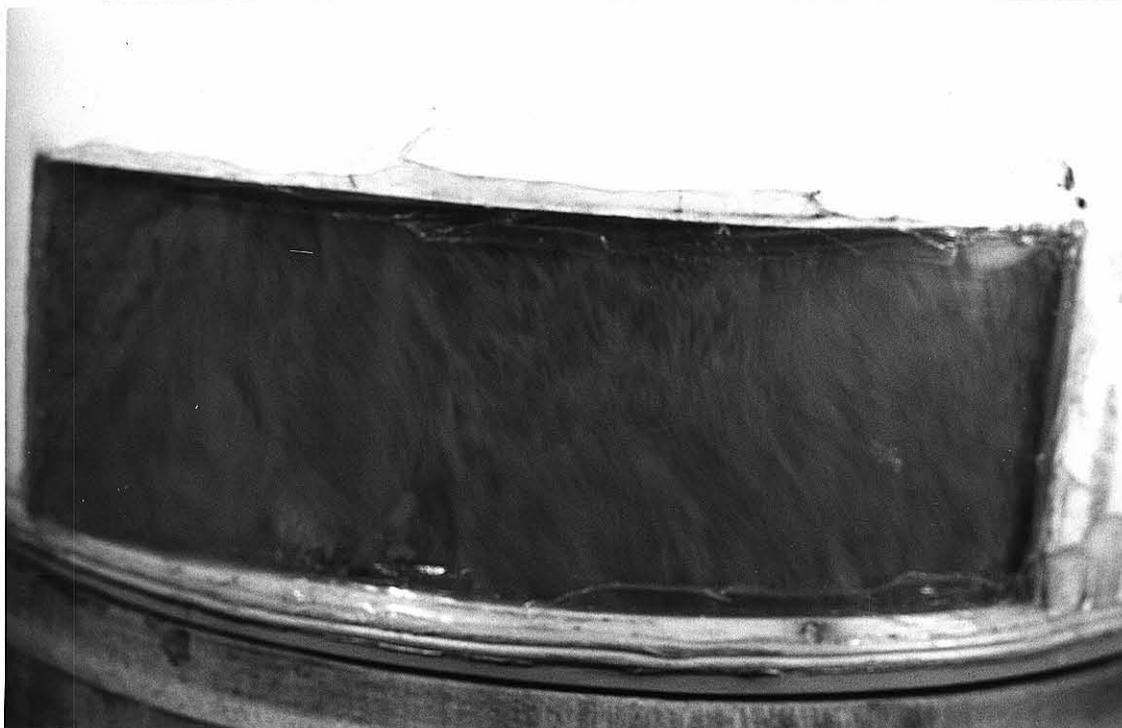
Fig. 20.   Horizontal mixing: 2800 rpm

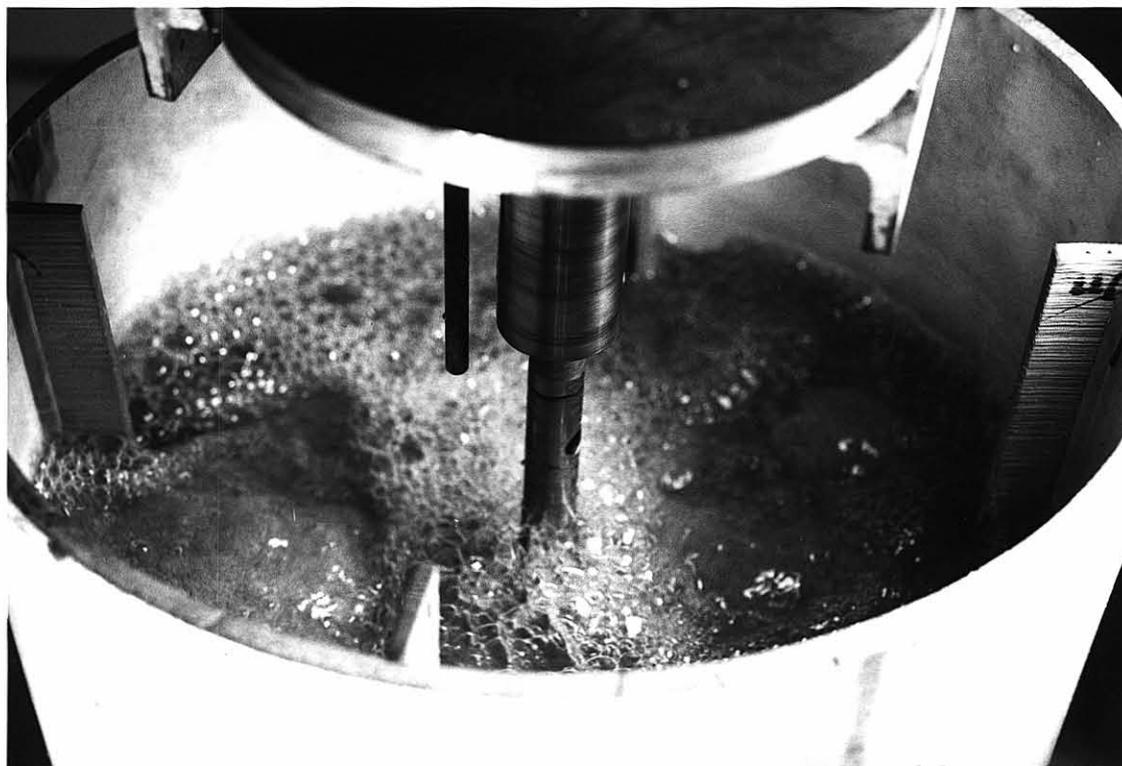Fig. 21.   Bubble formation: 270 rpm.

Fig. 22. Bubble formation: 500 rpm

Fig. 23. Bubble formation: 2800 rpm.
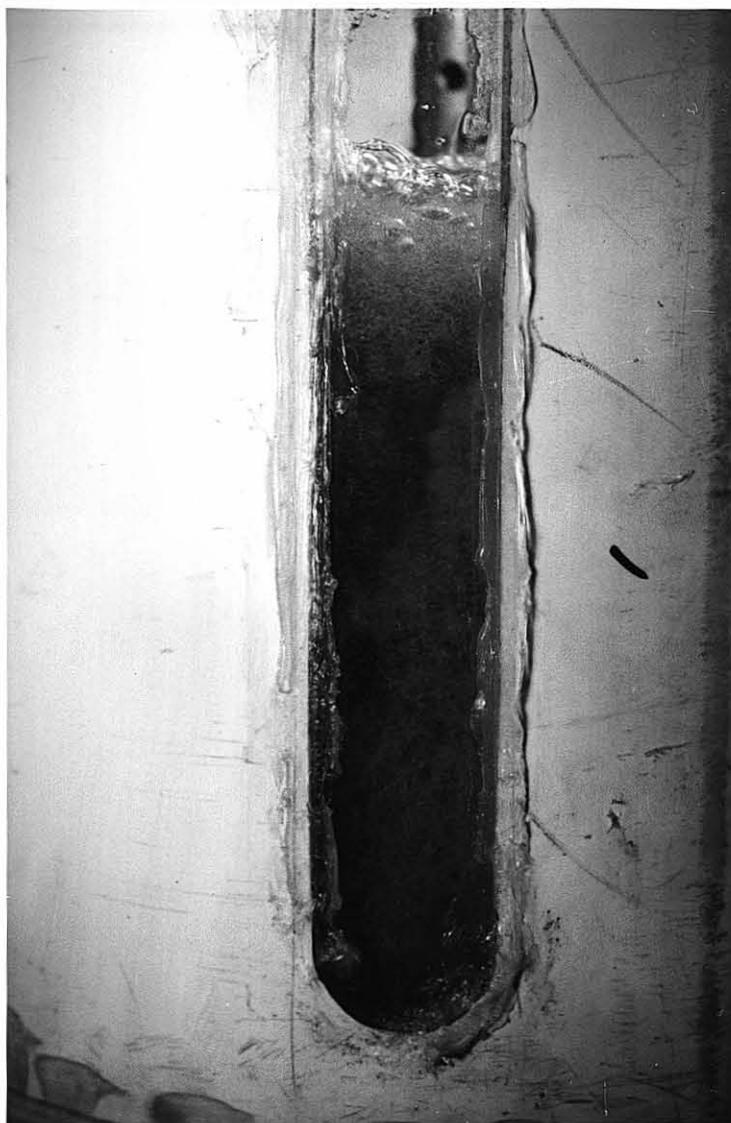
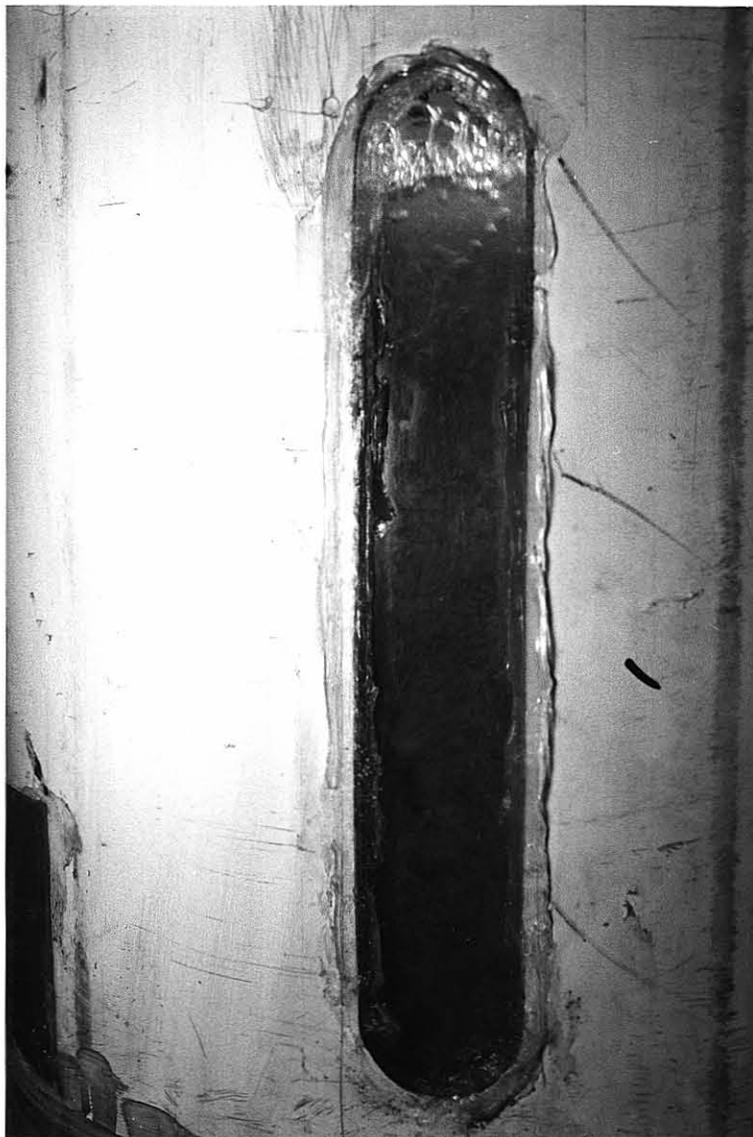- 32 -

Fig. 24. Vertical mixing: 270 rpm.

Fig. 25. Vertical mixing: 500 rpm.

Fig. 26. Vertical mixing: 2800 rpm.