DEVELOPMENT OF TECHNOLOGY

for the

PRODUCTION OF ELECTROLYTIC MAGNESIUM METAL

from

MAIN CREEK MAGNESITE

submitted by

GOLDEN TRIANGLE RESOURCES
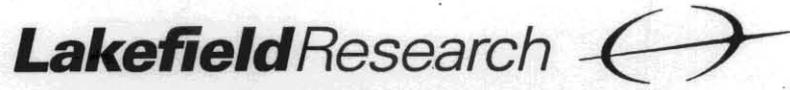
LR 5553 - Progress Report No. 1

NOTE: This report refers to the samples as received.
The practice of this Company in issuing reports of this nature is to require the recipient not to publish the report or any part thereof without the written consent of Lakefield Research.

Lakefield Research

185 Concession Street, Postal Bag 4300
Lakefield, Ontario, K0L 2H0
Tel: (705) 652-2024
Fax: (705) 652-1918
September 1, 1999

ABSTRACT

This report covers work done to evaluate the ability of technology for the dehydration of magnesium chloride, developed by Alcan International, to reject impurities other than water/oxygen from the dehydrated product. Six tests were done. A method supplied by Alcan International was followed. Three synthetic solutions, containing magnesium chloride and selected impurities at selected levels, were used. These solutions simulated liquor at three points in the envisaged flowsheet, viz.

After neutralization of excess acid in the leach liquor

After the removal of iron

After the removal of manganese

The starting solutions were evaporated to dryness, producing crystals of $MgCl_2.xH_2O$. The crystals were dissolved in methanol and the resulting methanol/water solutions were filtered. The filtrates were added to ammonia-saturated methanol to precipitate $MgCl_2.6NH_3$. The deportment of magnesium and the impurities was measured over each of the process steps.

The results produced were evaluated by dividing the ratios of impurities to magnesium by the corresponding ratios in the specifications for commercial magnesium metal or for anhydrous magnesium chloride suitable for feeding to magnesium electrolysis cells.

Some impurities were partially rejected and others were not. It is suggested that the brine entering the dehydration steps can and should be sufficiently purified to obviate the need for further removal of impurities other than water/oxygen in the dehydration section of the flowsheet.

826003

TABLE OF CONTENTS

01/09/99
Progress Report 1.doc
    LakefieldResearch
    iii

LIST OF TABLES

INTRODUCTION

Golden Triangle Resources NL intends to produce magnesium metal from magnesite, via a hydrometallurgical process route. The envisaged source of magnesite is the Main Creek deposit. Lakefield Research Limited carried out an initial program of work, the results of which form the basis of the envisaged process route[1]. It currently entails the leaching of Main Creek magnesite in hydrochloric acid, purification of the resulting solution, evaporation to yield $MgCl_2$ x H_2O and conversion of this hydrated magnesium chloride to anhydrous $MgCl_2.6NH_3$. This material is then calcined to anhydrous $MgCl_2$, from which magnesium metal is produced by molten-salt electrolysis.

Alcan International has done a substantial amount of laboratory-scale work on the production of dehydrated magnesium chloride that would be suitable feed material for their magnesium electrolysis technology. The emphasis was on the essentially complete removal of oxygen/water from the magnesium chloride. Pure chemicals were used, precluding any work on the deportment of impurities other than oxygen/water. This report covers tests done using synthesized solutions, representing liquors from three different points in the envisaged flowsheet, to examine the deportment of impurities other than oxygen/water in the section of the flowsheet in which the water and magnesium chloride are separated. That section of the flowsheet employs dehydration technology developed by Alcan International[2]. The $MgCl_2.xH_2O$ is dissolved in methanol, then the methanol/water solution of magnesium chloride is added, along with ammonium chloride, to ammonia-saturated methanol under an atmosphere of excess ammonia. This causes ammoniated magnesium chloride ($MgCl_2.6NH_3$) to precipitate. The precipitate is recovered (filtration or centrifugation) and washed with more ammonia-saturated methanol.

A separate report[5] covers the results of the scouting tests on flotation, also commissioned by Golden Triangle Resources NL, to examine the merits of flotation for the removal of calcium upstream of the main process circuit.

LAKEFIELD RESEARCH

C. A. Fleming, Ph.D.
Vice President and Chief Operating Officer

M. Dry, Ph.D.
Assistant Manager - Hydrometallurgy

Experimental testwork: J. Geldart, E. Majchrzak, L. Paquette
Report preparation: C. Pilley

SUMMARY

1. EXPERIMENTAL

Three solutions were synthesized from reagent-grade chemicals. They simulated (solids-free) liquor directly after the neutralization of excess acid in the magnesite leach liquor, after iron removal and after manganese removal. Table 1 shows the composition of the solutions. The suite of analyses was agreed at a meeting that was held at Lakefield Research Limited in June 1999. The synthetic solutions were evaporated to crystalline $MgCl_2.xH_2O$. Table 2 lists the composition of these crystals.

In total, six tests were done. Alcan International supplied the process conditions and the basic method that was tested[2]. The first three tests examined the methanol dissolution step. Samples of the crystals of hydrated magnesium chloride were dissolved in methanol and the resulting methanol/water solutions were filtered. The solid residues and methanol/water solutions were measured and analyzed. The last three tests examined the ammoniation step. In these tests, the crystals of hydrated magnesium chloride were dissolved in methanol and the methanol/water solutions were filtered. The solid residues from the methanol-dissolution step were sent for mineralogical examination, and the methanol/water solutions were added at a controlled rate to ammonia-saturated methanol, in a closed ammonia-sparged reactor. The resulting precipitate ($MgCl_2.6NH_3$) was filtered from the methanol/water mother liquor and washed with more ammonia-saturated methanol. The precipitate, filtrate and wash solutions were measured and analyzed. In some cases, secondary precipitation occurred in primary and wash filtrates. These secondary precipitates were filtered out, measured and also analyzed. Details of the experimental methodology used in the individual tests appear with the detailed experimental data, in Appendix I.

For continuity, the test numbering system from the previous work[1] was maintained in the present work. The test numbers therefore continue from where the previous work stopped.

Table 1: Composition of the synthesized solutions used in the Phase 2 work, mg/L

Element	Solution 1	Solution 2	Solution 3
Al	14	11	11
Ca	4300	985	1100
Cr	3.5	5.7	2.2
Cu	2.4	2.3	1.4
Fe	910	57	6.3
Mg	89 000	93 500	99 000
Mn	220	52	<0.5
Na	13	11	11
Ni	3.1	3.7	1.6
Zn	4.4	6.2	6.4
B	1.35	1.33	0.74
Si	17	3.4	3.2
S	22.9	1 060	1 060

Table 2: Composition of the hydrated magnesium chloride crystals, parts per million

Element	From solution 1	From solution 2	From solution 3
Al	30	25	23
Ca	5 900	1 700	1 600
Cr	7.6	13	5.4
Cu	<5	6.6	<5
Fe	1 200	120	14
Mg	130 000	160 000	160 000
Mn	290	110	<5
Na	21	33	24
Ni	6.9	6.3	<5
Zn	11	13	11
B	<5	<5	<5
Si	<200	<200	<200
S	100	1 100	1 100

2. RESULTS

Table 3 lists the composition of the methanol/water solutions obtained in the first three (methanol dissolution) tests. Table 4 lists the composition of the precipitates obtained from the last three (ammoniation) tests. Data on the composition and quantity of the residues from the dissolution of the hydrated magnesium chloride in methanol, and on the secondary precipitates from the various filtrates and wash solutions after crystallization, appear with the detailed experimental data in Appendix I. Filtration of the primary precipitates from the ammoniation step was rapid. Filtration of the methanol/water solutions was extremely slow. In the last three tests, the time taken for this filtration was recorded and found to be between 24 and 96 hours. The residues obtained in these tests were subjected to mineralogical examination. The mineralogical report appears in Appendix II. The residue from Test 43 (starting from Solution 1) was found to contain bischofite ($MgCl_2.6H_2O$) and ammonium magnesium chloride hydrate ($NH_4MgCl_3.6H_2O$). The residues from Tests 44 and 45 (starting from Solutions 2 and 3 - after iron and manganese removal, respectively) were found to contain mainly bischofite and magnesium sulphate hydroxide hydrate ($MgSO_4.zMg(OH)_2.xH_2O$), with minor amounts of ammonium magnesium chloride hydrate.

Magnesium dissolution percentages (based on the residues and filtrates) of 99, 94 and 96 were achieved in Tests 40, 41 and 42 respectively. Magnesium precipitation percentages of 87, 85 and 78 were achieved in Tests 43, 44 and 45 respectively.

The levels of some of the impurities in the methanol/water solutions and precipitates were below the detection limits of the analytical equipment used. These results are shown in Tables 3 and 4 as 'less than' (<) the relevant detection limits.

Table 3: Composition of the methanol/water solutions, mg/l

Element	Test 40	Test 41	Test 42
Al	<5	<5	<5
Ca	2 800	720	590
Cr	<1	<1	<1
Cu	1.9	2.7	1
Fe	370	<1	<1
Mg	59 000	73 000	71 000
Mn	130	46	<0.5
Na	<5	<5	<5
Ni	3.5	<1	<1
Zn	4.8	5.7	5.4
B	<1	<1	<1
Si	<5	<5	<5
S	7.2	53	430

Table 4: Composition of the precipitates, parts per million

Element	Test 43	Test 44	Test 45
Al	<200	<200	<200
Ca	365	260	320
Cr	<50	<50	<50
Cu	<20	<20	<20
Fe	273	<50	<50
Mg	241 000	202 000	215 000
Mn	570	120	<50
Na	<20	<20	<20
Ni	<20	<20	<20
Zn	20	20	20
B	<10	<5	<5
Si	<200	<200	<200
S	100	100	100

3. DISCUSSION

Oxygen and water cause adverse effects in magnesium electrolysis[3]. The separation of oxygen/water from magnesium chloride is the primary function of the Alcan dehydration technology. Appendix III contains an abstract of a technical report[2] on work done by Alcan International. Dehydrated magnesium chloride containing 0.1 mass percent MgO was produced. No other impurities were examined in that work. The oxygen specification for feed to the Alcan Multipolar Cell is 'less than' 0.1 mass percent MgO[2]. The following discussion covers the deportment of impurities other than oxygen/water in the dehydration technology developed by Alcan International.

3.1. Composition of the precipitates

The magnesium content of the precipitates (from the ammonia-saturated methanol) was found to be higher than that of $MgCl_2.6NH_3$, which would contain 12.3 percent Mg, as opposed to the 20 to 24 percent found in the precipitates. The difference can be ascribed to ammonia loss from the precipitates after their production. In the previous work[1] (page 7 of Appendix A3), a similar effect was observed. When the filtration was done under an atmosphere of ammonia, and the samples were taken and kept under ammonia, the Mg content of the precipitate was 12.8 percent and mineralogical examination showed no evidence of oxychlorate of hydroxychloride compounds. In the present work, filtration and sampling of the precipitates under ammonia was not necessary. The ratios of the various impurity elements to magnesium constitute the information required. The changes that the loss of ammonia caused to the mass of the precipitates would have altered the analyzed values of magnesium and impurity elements by the same factor, and would not affect the ratios of impurity to magnesium in any way.

3.2. Filtration

The observed rates of filtration of the methanol/water solutions require comment. If the observed filtration times (about 24 hours for Test 43, about 96 hours for Tests 44 and 45) are representative of what would happen in full-scale practice, the inclusion of

these filtration steps will most probably not be possible. The results of this work show that, except for calcium, the magnesium chloride brine can be made sufficiently pure to eliminate the need for the dehydration section of the flowsheet to reject any impurities other than oxygen/water. Also, calcium was not found to any significant extent in the residues from the dissolution tests. Filtration of the methanol/water solution should be unnecessary, unless it is required to separate out minor amounts of magnesium oxide. Appropriate attention should be paid to this aspect of the process when process optimization work is done.

The source of the ammonium ion in the $NH_4MgCl_3.6H_2O$ found in the residues from the methanol-dissolution tests is not immediately apparent. Traces of atmospheric ammonia in the laboratory may have reached the methanol/water solutions, or more probably the residues, and reacted with the magnesium chloride. The formation of magnesium sulphate hydroxide hydrate probably occurred as a result of the higher levels of sulphate in Solutions 2 and 3. These solutions were synthesized that way because it was assumed at the time that calcium would be removed from the solution via the addition of sulphate to precipitate calcium sulphate. This is most probably no longer the case, because the use of carbon dioxide to precipitate calcium carbonate is considered to be a better option. The presence of bischofite ($MgCl_2.6H_2O$) in the residues is possibly due to methanol/water solution that was retained in the residues, then evaporated during the drying of the samples.

3.3. Deportment of impurities

This work was done primarily to determine the ability of the Alcan dehydration technology to reject impurities while separating water from magnesium chloride. Realistically, no impurity will go to a level of absolute zero. If the ratio of any given impurity to magnesium is at or below the level at which the final magnesium metal remains 'on specification' (even if all of the impurity ends up in the metal) and the electrolysis operation is unaffected, the importance of that particular impurity falls away. It is therefore appropriate to relate the experimental results emanating from this work to the impurity to magnesium ratios required, either for satisfactory electrolysis or to

achieve the specifications for magnesium metal. Table 5 lists the relevant specifications for magnesium metal and electrolysis feed (anhydrous magnesium chloride) that have been uncovered to date.

Table 5: Impurity limits for magnesium metal and/or electrolysis feed, mass percent

Element	Electrolysis feed[3]	Commercial metal[4]
Al	0.008	0.05
Ca	0.02	0.01
Cr	0.008	0.01
Cu	0.008	0.02
Fe	0.008	0.01
Mn	0.016	0.1
Na	0.06	
Ni	0.0003	0.002
Zn	0.008	0.05
B	0.001	
Si		0.05
S	0.1	

Calcium, sodium, potassium and fluoride do not interfere directly with the electrolysis of magnesium. (The molten electrolyte typically contains about 20 - 25 percent $CaCl_2$ and 55 percent NaCl. Calcium fluoride is used as a flux. Potassium is a constituent of carnalite, which is also used as feed for magnesium electrolysis.) The impact of these impurities is indirect, in that their concentrations have to be controlled by a bleed of the electrolyte, which impacts on the process economics. In magnesium electrolysis, some of the molten salt electrolyte is entrained in the molten magnesium metal that is tapped from the electrolysis cells. Depending on the technique used, between 1 and 2 percent of the volume tapped as metal is entrained electrolyte[3].

The electrolyte contains about 20 percent by mass of calcium chloride. Assume a volume of entrained electrolyte of one percent of the volume of the tapped metal. The densities (expressed as specific gravity) of the molten metal and the molten electrolyte are 1.55 and 1.73 respectively[3]. This implies that, for each 100 kilograms of anhydrous magnesium chloride (containing 25.5 kilograms of magnesium) fed to electrolysis, about 0.02 kilograms of calcium leave as entrained electrolyte. About 0.02 kilograms of calcium can therefore enter in the feed. This gives a permissible calcium level of about 0.02 percent in the anhydrous magnesium chloride. A similar argument gives a level of about 0.06 percent for sodium.

A set of target impurity to magnesium ratios can be derived by dividing the impurity limits in Table 5 by 99.8 (the minimum allowable percentage of Mg in commercial magnesium metal[4]), or by 25.5 (the theoretical mass percentage of Mg in $MgCl_2$), depending on the particular specification. The target ratio for any given impurity would be the lower number.

Dividing the impurity to magnesium ratios measured in the starting solutions, hydrated magnesium chloride, methanol/water solutions and precipitates by the target impurity to magnesium ratios shows whether or not the various solutions and solids are of suitable purity for the production of magnesium metal. If the relevant index (ratio divided by target ratio) is less than unity, the impurity in question is at a sufficiently low level. Tables 6 to 8 show these indices. Where an impurity level is a 'less than' number, the corresponding index is shown as 'less than' the value at the detection limit concerned.

3.3.1. Sulphur

The results of Tests 40/43 (starting from Solution 1) show no rejection of sulphur. The sulphur to magnesium indices in these two tests were below unity throughout, meaning that sulphur is unlikely to be a problem at the level used in Solution 1. Solutions 2 and 3 were formulated on the assumption that sulphate would be added to remove calcium, *via* the precipitation of gypsum, in the overall process. The results of Tests 41/44 and 42/45 show a rejection of sulphur, although they give conflicting

evidence on where the rejection occurred. However, the conflict is not important, because the removal of calcium *via* the addition of sulphate to precipitate calcium sulphate has been supplanted by the addition of carbon dioxide to precipitate calcium carbonate. These arguments lead to the conclusion that it will not be necessary to rely on the dehydration steps for sulphur rejection.

Table 6: Impurity to magnesium indices
(tests starting from solution 1)

Element	Solution 1	MgCl2.xH₂O	Methanol/water	Precipitate
Al	0.5	0.8	<0.3	<3
Ca	62	59	61	2
Cr	0.1	0.2	<0.06	<0.7
Cu	0.2	<0.3	0.3	<0.7
Fe	34	30	21	37
Mn	4	4	4	4
Na	0.06	0.07	<0.04	<0.04
Ni	3	4	5	<7
Zn	0.2	0.3	0.3	<0.3
B	0.4	<1	<0.4	<1
Si	0.4	<3	<0.2	<2
S	0.07	0.2	0.03	0.1

Table 7: Impurity to magnesium indices (starting from Solution 2)

Element	Solution 2	MgCl2.xH$_2$O	Methanol/water	Precipitate
Al	0.4	0.5	<0.2	<3
Ca	13	14	13	2
Cr	0.2	0.3	<0.04	<0.8
Cu	0.2	<0.3	0.3	<0.8
Fe	2	2	<0.04	<0.8
Mn	0.9	1	1	1
Na	0.05	0.09	<0.03	<0.04
Ni	3	3	<1	<8
Zn	0.2	0.3	0.3	0.3
B	0.4	<0.8	<0.4	<0.6
Si	0.07	<3	<0.1	<2
S	3	2	0.2	0.1

Table 8: Impurity to magnesium indices (starting from Solution 3)

Element	Solution 3	MgCl2.xH$_2$O	Methanol/water	Precipitate
Al	0.4	0.5	<0.2	<3
Ca	14	13	11	2
Cr	0.07	0.1	<0.05	<0.8
Cu	0.1	<0.3	0.1	<0.8
Fe	0.21	0.3	<0.05	<0.8
Mn	<0.01	<0.05	<0.01	<0.4
Na	0.05	0.06	<0.03	<0.04
Ni	1	<3	<1	<8
Zn	0.2	0.2	0.3	0.3
B	0.2	<0.8	<0.4	<0.6
Si	0.06	<3	<0.1	<2
S	3	2	2	0.1

3.3.2. Iron and manganese

There was no significant reduction in the iron to magnesium index in the tests starting from solution 1 (before iron removal). The results for solutions 2 and 3 indicate some rejection of iron over the methanol-dissolution step, but no rejection of manganese. The iron to magnesium and manganese to magnesium indices came out well below unity in the tests starting from solution 3 (after manganese removal). This shows that manganese removal, and therefore also iron removal, is appropriate in the aqueous circuit, upstream of the dehydration steps. This being so, there is no need for the dehydration steps to reject either iron or manganese.

3.3.3. Nickel

The nickel to magnesium index is above or near to unity in all the results. However it is below ten throughout. The starting solutions were synthesized with ten times the nickel that was measured in the previous work[1], because it would have been excessively difficult to make up solutions with lower nickel levels, due simply to the impurity levels of the available reagents. Even though the results of this work indicate no significant rejection of nickel, the iron and manganese removal steps can be made to remove nickel as well. In reality, therefore, nickel is unlikely to present a problem.

3.3.4. Boron and silicon

The boron to magnesium and silicon to magnesium indices indicate some rejection of boron and silicon, but more work would be required to verify this. For Solutions 1, 2 and 3 and the corresponding methanol/water solutions, the indices for these two elements are well below unity. The Si indices for the hydrated crystals and the precipitate are 'less than' 3 and 2 respectively. However, since matter is not created or destroyed chemically, the actual ratios of silica to magnesium in the hydrated crystals and precipitates must be similar to those measured in the solutions. The same argument holds for boron. There appears to be little need for the dehydration steps to reject either boron or silicon.

3.3.5. Aluminium and chromium

The indices for aluminium and chromium could be said to indicate some rejection

of these elements. Again, however, the indices are below unity throughout, indicating that there is no need for the dehydration steps to reject aluminium or chromium. These elements can be very effectively removed in the upstream iron removal step, should that be necessary.

3.3.6. Copper and zinc

The indices for copper and zinc show no rejection of these elements, but are well below unity throughout. There is therefore no need for the dehydration steps to reject copper or zinc.

3.3.7. Calcium and sodium

The indices for sodium are below unity throughout, showing that the Alcan dehydration technology does not need to reject sodium. There does appear to be some rejection of calcium over the precipitation step. If such rejection is shown to be important, it will be necessary to consider the impact of recycled calcium (with the ammonium chloride) in the dehydration section of the flowsheet. However, the indices for calcium in the precipitates all came out at 2, even though the levels of calcium in the three methanol/water solutions were 2 800, 720 and 590 parts per million respectively. It may be that calcium rejection in the precipitation step is not a function of the amount of calcium in the methanol/water solution. For the starting solutions tested, the dehydration steps did not reject calcium sufficiently to sustain an electrolyte loss from the electrolysis cells of 1 percent (by volume) of the molten metal. A loss of about 2 percent would be required, if the level of calcium in the purified brine remains at the levels tested in the present work. If the rejection of calcium remains independent of the ratio of calcium to magnesium in the purified brine as the level of calcium is reduced, the 'target' for future tests on the precipitation of calcium carbonate could be a calcium to magnesium ratio as low as 0.0002. (About 14 parts per million of calcium, if the magnesium concentration is 70 grams per litre.) Alternatively, a greater loss of molten electrolyte might be preferable if the associated cost is less than that of producing very low levels of calcium in the purified brine.

CONCLUSIONS

The results of the present work, and the results reported by Alcan International[2], reveal no significant technical flaws in the envisaged flowsheet for the production of magnesium metal from Main Creek magnesite. The results of the present work lead to the following conclusions.

➢ The deportment of magnesium to the methanol/water solution was 99 percent for Solution 1. For solutions 2 and 3 it was 94 and 96 percent respectively. The higher sulphur level in Solutions 2 and 3 gave rise to more solid residue, and hence a greater loss of magnesium. The addition of sulphate, to remove calcium as calcium sulphate, has been changed to the addition of carbon dioxide, to remove calcium as calcium carbonate. The higher losses of magnesium found for Solutions 2 and 3 are therefore no longer relevant.

➢ The deportment of magnesium to the precipitated $MgCl_2.6NH_3$ was between 82 and 75 percent. Any magnesium that is not precipitated will probably need to be recycled to the crystallization step with the ammonium chloride. This implies a circulating load of magnesium, which may impact on the water balance of the dehydration section.

➢ The Alcan dehydration technology might reject some calcium, sulphur, boron and silicon. However, except for calcium, the results also show no real need for such rejection, as the ratios of these elements to magnesium were found to be below those required for the production of commercial magnesium metal.

➢ The purified brine needs to contain less calcium than the solutions used in the present work. Alternatively, the process will need to tolerate a loss (or a recycle to an appropriate point in the flowsheet) of molten electrolyte of about 2 percent (by volume) of the molten metal tapped from the electrolysis cells.

➢ Filtration of the methanol/water solutions was found to be extremely slow. No significant deportment of impurities to the residue from the methanol-dissolution step

was observed. This means that the filtration of the methanol/water solutions will probably not be necessary.

RECOMMENDATIONS

Further development and optimization of the flowsheet for the production of magnesium metal from Main Creek magnesite should address the following recommendations, which arise from the results of the present work.

➤ The impact of a circulating load of magnesium chloride in the dehydration section of the flowsheet should be assessed. Tests aimed at increasing the extent of 'first-pass' precipitation of the $MgCl_2.6NH_3$ should also be done.

➤ The dehydration steps should be used to remove oxygen/water. The other impurities should be removed upstream. If higher-grade magnesium metal is required, additional purification steps should be added to the aqueous part of the flowsheet (e.g. ion exchange to remove boron). It is suggested that this would be better than attempting to use the dehydration steps for more than the rejection of oxygen/water, which is the primary function of the Alcan dehydration technology.

➤ The appropriate economic calculations should be done and the calcium-removal target for future work on the precipitation of calcium carbonate should be set accordingly.

➤ Tests should be done to determine whether or not filtration of the methanol/water solution is necessary.

REFERENCES

1. Experimental Development of a Process to Produce Magnesium from MC36 Magnesite Ore. Final Report (Progress Report #4) on project number 5398, April 6, 1999, Lakefield Research Limited.

2. Confidential report supplied to Lakefield Research Limited under cover of a secrecy agreement between Alcan International and Lakefield Research Limited.

3. Information received from Alcan International, under cover of a secrecy agreement between Alcan International and Lakefield Research Limited.

4. Metal specifications from Timminco, supplied to Lakefield Research Limited by Andrew Firek, consultant to Golden Triangle Resources NL.

5. The Removal of Dolomite from a Magnesite Ore Sample submitted by Golden Triangle Resources N.L. LR 5519 Progress Report No. 1, August 24, 1999.

Appendix I

Detailed experimental results

Methanol dissolution : Experimental method

Feed: Tests 40 and 43 - Crystals from Solution 1
              Tests 41 and 44 - Crystals from Solution 2
              Tests 42 and 45 - Crystals from Solution 3

Procedure:
1. 100 (Tests 40 - 42) or 200 (Tests 43 - 45) grams of analytical grade methanol was placed in a 200 (Tests 40 - 42) or 400 (Tests 43 - 45) ml beaker.
2. 54 (Tests 40 - 42) or 108 (Tests 43 - 45) grams of $MgCl_2 \cdot 6H_2O$ crushed crystals were added.
3. The solution was mixed using mechanical agitation.
4. After 30 minutes (60 for Test 44), the solution was filtered on 0.45 micron filter paper. No wash was applied.

Observations :

Test No.	Dissolving Time (minutes)	* Filtration Time (hours)	Filtrate Volume (mL)	Filtrate Colour	Residue Weight (g)	Residue Colour
43	~ 30	~ 24	260	yellow/brown	0.50	red/brown
44	~ 60	~ 96	156	clear, no colour	3.18	creamy/white
45	~ 30	~ 96	126	clear, no colour	3.10	creamy/white

* using 0.45 um mixed cellulose ester paper (47 mm)

Ammonia precipitation : Experimental method

Procedure:
1. 400mL of analytical grade methanol and 4.36 g ammonium chloride were placed in a 1L reaction vessel. The vessel was placed in a water bath at 20°C. Anhydrous ammonia was sparged into the methanol at 200 ml/min to saturate it.
2. After saturation, the ammonia flowrate was increased to 1100 ml/min.
3. The feed solution was then pumped into the saturated methanol over a 2 hour period
4. Ammonia was continuously sparged into the pulp over the entire test period.
6. After 2 hours, the slurry was filtered and washed with ammonia-saturated methanol.

Test 40

Metallurgical Balance :

Product	Amount (mL, g)	Assays (mg/L, %)												
		Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
In :														
MgCl$_2$.xH$_2$O	54	13.0	0.59	0.01	0.12	0.029	0.001	0.001	<0.02	0.003	<5ppm	<5ppm	0.001	0.002
Out :														
Residue	0.63	13.0	0.550		5.500	0.038								
Filtrate	112	59000	2800	7.2	370	130	3.5	4.8	<5	<5	1.9	<1	<1	<5

Product	Distribution (%)												
	Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
Residue	1	1		46	2								
Filtrate	99	99	100	54	98	100	100						

Accountability, % (Total out/Total in)												
Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
95	100	15	117	95	105	91						

Test 41

Metallurgical Balance :

Product	Amount (mL, g)	Assays (mg/L, %)												
		Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
In :														
MgCl$_2$.xH$_2$O	54	16.0	0.17	0.01	0.01	0.011	0.001	0.001	<0.02	0.003	0.001	<5ppm	0.001	0.003
Out :														
Residue	3.08	16.0	0.480		0.260	0.019								
Filtrate	100	73000	720	53	<1	46	<1	5.7	<5	<5	2.7	<1	<1	<5

Product	Distribution (%)												
	Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
Residue	6	17		100	11								
Filtrate	94	83	100		89		100			100			

Accountability, % (Total out/Total in)												
Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
90	95	98	124	87		81			76			

Test 42

Metallurgical Balance :

Product	Amount (mL, g)	Assays (mg/L, %)												
		Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
In :														
MgCl$_2$.xH$_2$O	54	16.0	0.16	0.11	0.001	<5	<5	0.001	<0.02	0.002	<5	<5	0.001	0.002
Out :														
Residue	1.83	17.0	0.960		0.046	0.001								
Filtrate	102	72500	600	430.0	<1	<0.5	<1	5.4	<5	<5	1	<1	<1	<5

Product	Distribution (%)												
	Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
Residue	4	22		100									
Filtrate	96	78	100				100						

Accountability, % (Total out/Total in)												
Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
89	91	74	111			93						

Test 43

Observations:

The preg and wash solutions were filtered on #541 filter paper. A white precipitate formed after solutions had sat overnight. The solutions were refiltered using the 0.45 um cellulose paper. The precipitate from the preg and wash solutions were also submitted for analyses.

Metallurgical Balance :

Product	Amount (mL, g)	Assays (mg/L, %)												
		Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
In :														
MgCl$_2$.xH$_2$O	108	13.0	0.59	0.01	0.12	0.029	0.001	0.001	<0.02	0.003	<5ppm	<5ppm	0.001	0.002
Out :														
Methanol residue	0.5	21	0.85	<0.01	8.3	0.050	0.022	0.004		0.40	0.028		0.13	0.053
Filtrate	470	3390	1100	9.46	<1	<2		<0.5	<5	<5	<1	<1	<1	<5
Wash	210	1620	510	11.9										
Filtrate residue	1.01	24.3	4.42	0.01	0.421	0.024	< 0.002	0.004	< 0.02	< 0.02	< 0.002	<10 ppm	0.01	< 0.002
Wash residue	2.25	31.9	0.478	0.04	0.032	0.057	< 0.002	0.016	< 0.02	< 0.02	< 0.002	<10 ppm	< 0.005	0.005
Precipitate	54.5	24.9	0.036	< 0.01	0.273	0.057	< 0.002	0.002	< 0.02	< 0.02	< 0.002	<10 ppm	< 0.005	< 0.002

Product	Distribution (%)												
	Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
Methanol residue	1	1		21	1		1					87	70
Filtrate	10	74	56										
Wash	2	15	31										
Filtrate residue	1	6	1	2	1		3					13	
Wash residue	4	2	11	0	4		24						30
Precipitate	82	3		76	95		72						

Accountability, % (Total out/Total in)												
Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
118	110	74	151	105	15	127		62			91	17

Test 44

Observations:

The preg and wash solutions were filtered on #541 filter paper. The solutions were then refiltered using the 0.45 um cellulose paper. All residues were combined for analyses.

Metallurgical Balance:

Product	Amount (mL, g)	Assays (mg/L, %)												
		Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
In :														
MgCl$_2$.xH$_2$O	108	16.0	0.17	0.11	0.01	0.011	0.001	0.001	<0.02	0.003	0.001	<5ppm	0.001	0.003
Out :														
Methanol residue	3.18	16	0.51	2.1	0.43	0.046	0.026	0.001		0.057	0.003		0.037	0.019
Filtrate	340	3470	237	<10	<1	0.74		<0.5	<5	<5			<1	<5
Wash	120	1990	929	<10	<1	0.64		<0.5	<5	<5	<1	<1	<1	<5
Precipitate	41.4	20.2	0.026	0.01	< 0.005	0.012	< 0.002	0.002	< 0.020	< 0.020	< 0.002	<5 ppm	< 0.005	< 0.002

Product	Distribution (%)												
	Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
Methanol residue	5	7	94		22		3						
Filtrate	11	37			4								
Wash	2	51			1								
Precipitate	81	5	6		73		97						

Accountability, % (Total out/Total in)												
Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
60	119	58	106	57	122	61		67	15		84	17

Test 45

Observations:

The preg and wash solutions were filtered on #541 filter paper. The solutions were then refiltered using the 0.45 um cellulose paper. All residues were combined for analyses.

Metallurgical Balance:

Product	Amount (mL, g)	Assays (mg/L, %)												
		Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
In :														
MgCl$_2$.xH$_2$O	108	16.0	0.16	0.11	0.001	<5	<5	0.001	<0.02	0.002	<5	<5	0.001	0.002
Out :														
Methanol residue	3.1	15.0	0.51	3.1	0.0003	0.001	0.008	<5 ppm		0.050	0.002		0.011	0.017
Filtrate	360	5790	252	<10	<1	<0.5		<0.5	<5	<5	<1	<1	<1	<5
Wash	190	1970	62	<10	<1	<0.5		<0.5	6.38	<5	<1	<1	<1	<5
Precipitate	41.4	21.5	0.032	0.01	< 0.005	< 0.005	< 0.002	0.002	<0.02	<0.02	<0.002	<5 ppm	<0.005	<0.002

Product	Distribution (%)												
	Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
Methanol residue	4	12	96										
Filtrate	18	69											
Wash	3	9											
Precipitate	75	10	4										

Accountability, % (Total out/Total in)												
Mg	Ca	S	Fe	Mn	Ni	Zn	Si	Al	Cu	B	Cr	Na
68	76	83	1			70		62			58	20

Appendix II

Mineralogical Report

Client: Golden Triangle Resources
LRL Project: 5398, LIMS # AUG4504.R99

Lakefield Research Limited
10-Aug-99

Summary of Qualitative X-ray Diffraction Results

Sample	Crystalline Mineral Assemblage (relative proportions based on peak height)			
	Major	Moderate	Minor	Trace
Dissolution Residue:				
5398-43	bischofite	ammonium magnesium chloride hydrate	-	-
5398-44	bischofite, *magnesium sulfate hydroxide hydrate	-	ammonium magnesium chloride hydrate	-
5398-45	bischofite, *magnesium sulfate hydroxide hydrate	-	ammonium magnesium chloride hydrate	-

*Tentative identification due to low concentrations, diffraction line overlap or poor crystallinity

Instrument:	Siemens D5000 diffractometer
Scan Conditions:	Co radiation, graphite monochromator, 40Kv, 30mA, Step: .04°, Step time: 1.0 s
Interpretations:	JCPDS / ICDD powder diffraction files. Siemens Search / Match software.
Detection Limit:	0.5-2%. Strongly dependent on crystallinity.

Interpretations do not reflect the presence of non-crystalline / amorphous compounds. Mineral proportions are based on relative peak heights and may be strongly influenced by crystallinity, structural group or preferred orientations.

Interpretations and relative proportions should be accompanied by supporting petrographic and geochemical data (WRA, ICP-OES).

Mineral	Composition
Ammonium Magnesium Chloride hydrate	$NH_4MgCl_3.6H_2O$
Bischofite	$MgCl_2.6H_2O$
Magnesium Sulfate Hydroxide hydrate	$MgSO_4.zMg(OH)_2.xH_2O$

Note:

The residues could not be separated from the millipore filters. The filters and residues were pulverized by hand, using a mortar and pestle. Residues 44 and 45 became moist and sticky as they were pulverized.
The diffraction pattern for Residue 45 appears to be shifted, possibly due to sample preparation technique.
The samples exhibited very poor crystallinity - relative mineral proportions were difficult to determine.
The main peak of magnesium sulfate hydroxide hydrate overlaps with ammonium magnesium chloride hydrate.

Lisa Ryan
XRD Technician
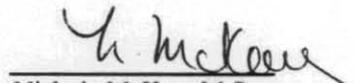
Nichola McKay, M.Sc.
Senior Mineralogist

Dissolution Residue 5398-43
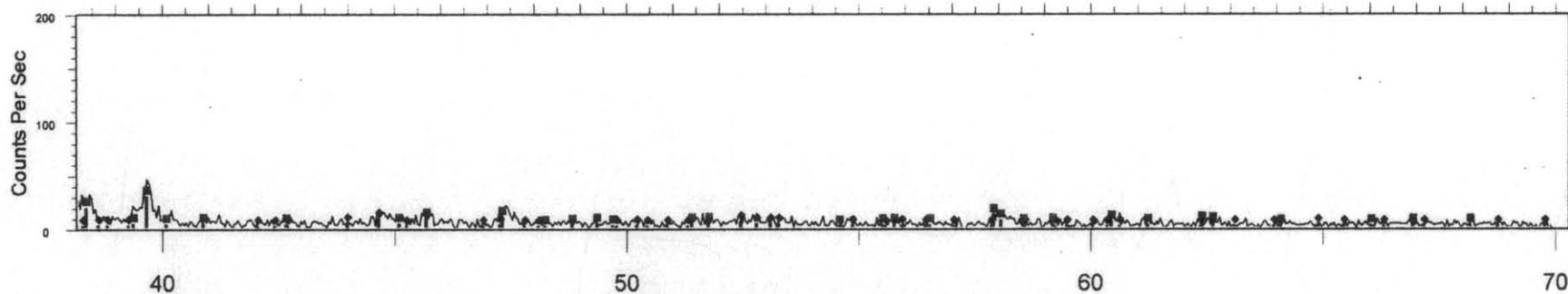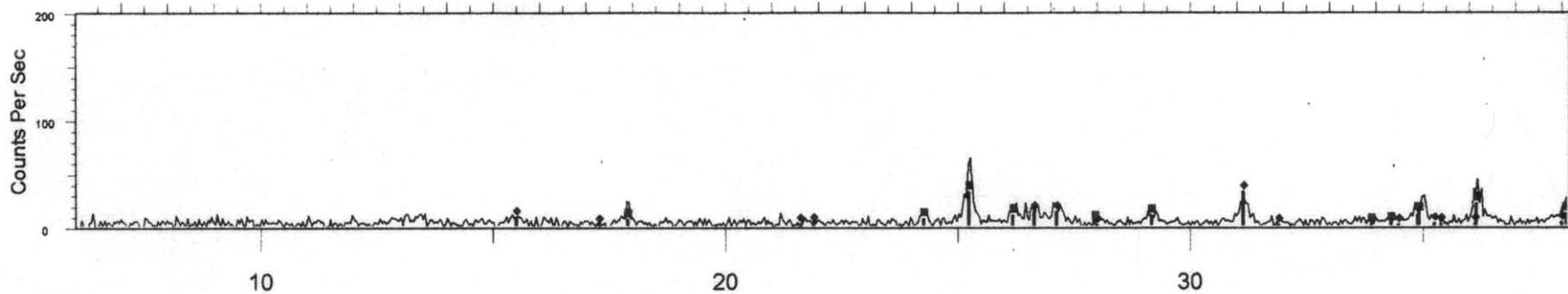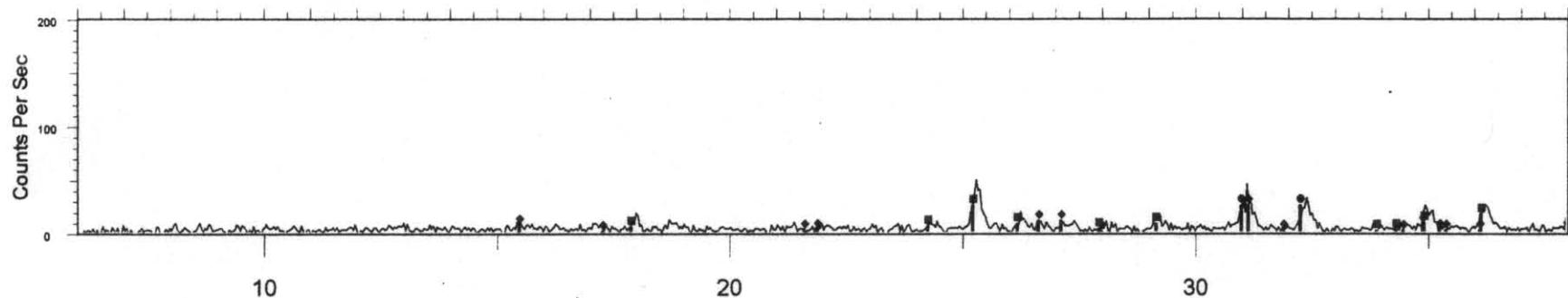

Lakefield Research Limited

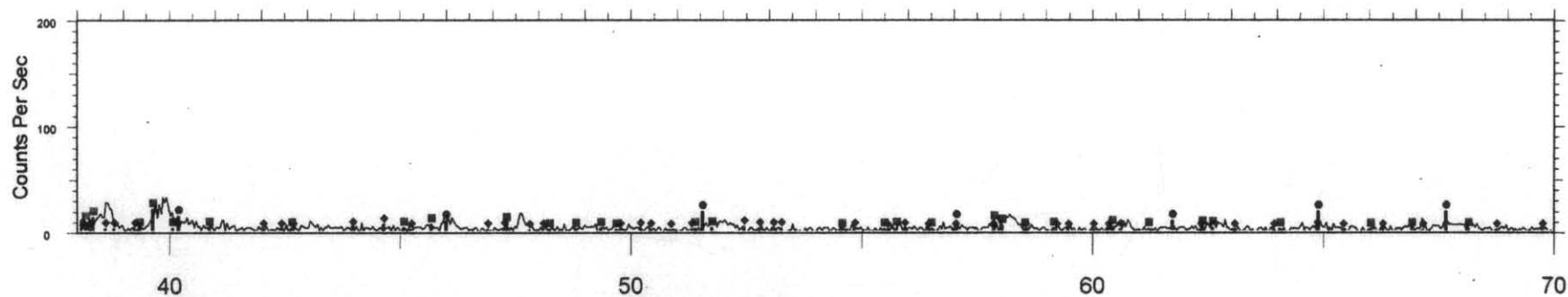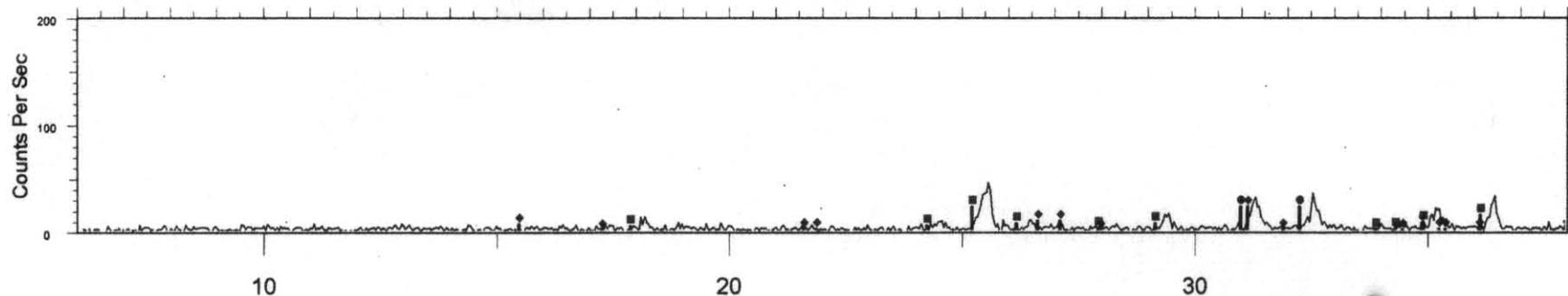- ⋀ File: aug4504-1.RAW - Start: 6.000 ° - End: 70.000 ° - Step: 0.040 ° - Step time: 1.0 s
- ■ 25-0515 (*) - Bischofite, syn - MgCl2·6H2O
- ◆ 25-0039 (I) - Ammonium Magnesium Chloride Hydrate - NH4MgCl3·6H2O

5 cm

Dissolution Residue 5398-44
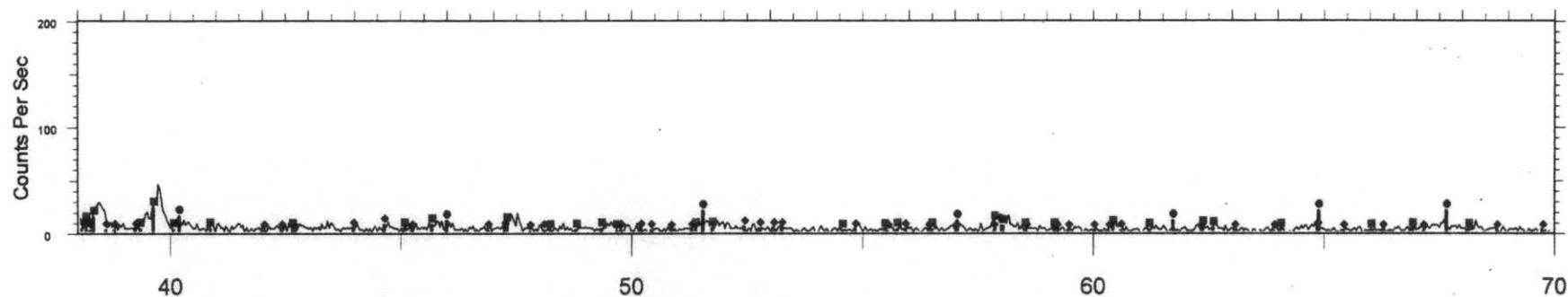
Lakefield Research Limited

File: aug4504-2.RAW - Start: 6.000 ° - End: 70.000 ° - Step: 0.040 ° - Step time: 1.0 s
25-0039 (I) - Ammonium Magnesium Chloride Hydrate - $NH_4MgCl_3 \cdot 6H_2O$
25-0515 (*) - Bischofite, syn - $MgCl_2 \cdot 6H_2O$
34-1051 (Q) - Magnesium Sulfate Hydroxide Hydrate - $MgSO_4 \cdot zMg(OH)_2 \cdot xH_2O$

5 cm

Dissolution Residue 5398-45

Lakefield Research Limited

⩗ File: aug4504-3.RAW - Start: 6.000 ° - End: 70.000 ° - Step: 0.040 ° - Step time: 1.0 s
● 34-1051 (Q) - Magnesium Sulfate Hydroxide Hydrate - MgSO4·zMg(OH)2·xH2O
■ 25-0515 (*) - Bischofite, syn - MgCl2·6H2O
◆ 25-0039 (I) - Ammonium Magnesium Chloride Hydrate - NH4MgCl3·6H2O

5 cm

APPENDIX III
Abstract of the report on work done by Alcan International

ALCAN DEHYDRATION TECHNOLOGY

The technology developed by Alcan International for the dehydration of $MgCl_2.xH_2O$ has four steps, *viz.*

- Dissolution of the $MgCl_2.xH_2O$ in methanol
- Crystallization of $MgCl_2.6NH_3$
- Filtration and washing of the $MgCl_2.6NH_3$
- Calcination to $MgCl_2$

This abstract presents an overview of the report on the laboratory testwork done by Alcan to determine the process conditions for each of the above steps. A copy of the 'contents' list of the report is shown to give an impression of the 'size' of the Alcan report.

1. *Dissolution of MgCl₂.xH₂O*

Samples of $MgCl_2.xH_2O$, $(2<x<10)$ were dissolved in methanol. Figure 2.1 shows the amounts of methanol required to dissolve $MgCl_2.xH_2O$, as a function of the value of x. The total solvent requirement is minimized for values of x between 6 and 10.

2. *Crystallization of MgCl₂.6NH₃*

The NH_4Cl is added to suppress the hydrolysis of Mg^{2+} during the crystallization of $MgCl_2.6NH_3$. (The resulting $Mg(OH)_2$ puts oxygen into the final product.) Figure 2.2 shows the effect of adding ammonium chloride to the solubility of $MgCl_2.xH_2O$ in methanol. The hydrolysis reaction is also suppressed by keeping the methanol/water weight ratio above about 3. Adding ammonia to the solution of magnesium chloride in methanol/water causes the precipitation of $MgCl_2.6NH_3$. Figure 2.3 shows the total reagents needed to produce crystallized $MgCl_2.6NH_3$ from $MgCl_2.xH_2O$, as a function of the amount of water with the hydrated magnesium chloride. The minimum appears to lie between four and six

waters of hydration in the $MgCl_2.xH_2O$. Figure 2.4 shows the effect of adding various levels of ammonium chloride to the crystallizer, on the MgO content of the calcined product. (There were some tricks to the calcination step that had not yet been learned at the time this data was generated. Subsequently, a final MgO content of <0.2% was achieved at a NH_4Cl/H_2O weight ratio of 0.13.) Figure 2.5 shows the effect of the methanol/water ratio on the solubility of magnesium chloride in ammonia-saturated methanol/water. Figure 2.6 shows the effect of the crystallization temperature on the quality of the anhydrous magnesium chloride. Photomicrographs of the precipitated $MgCl_2.6NH_3$ are appended.

3.   *Filtration and washing*

Wash volumes of between 2 and 46 milliliters of ammonia-saturated methanol per gram of $MgCl_2.6NH_3$ were tested. Over this range, final product purity was unaffected.

4.   *Calcination*

The calcination reaction was found to proceed in three distinct stages, as follows.

$MgCl_2.6NH_3 \rightarrow MgCl_2.2NH_3 + 4NH_3$ (Onset 150 ^{0}C, range 150 – 250 ^{0}C)

$MgCl_2.2NH_3 \rightarrow MgCl_2. NH_3 + NH_3$ (Onset 290 ^{0}C, range 290 – 350 ^{0}C)

$MgCl_2. NH_3 \rightarrow MgCl_2 + NH_3$ (Onset 380 ^{0}C, range 380 – 430 ^{0}C)

Heating rates of between 5 and 25 ^{0}C/minute were tested. The lowest MgO value in the calcined $MgCl_2$ (<0.2 mass %) was obtained at the lower heating rates, heating the material to 400 – 500 ^{0}C in an atmosphere of ammonia. Towards the end of the testwork, Alcan discovered that, if the calcination was done under the correct conditions, MgO levels of as low as 0.1 mass % could be achieved with methanol/water molar ratios as low as 1:1 in the crystallizer. This could significantly reduce the solvent usage in the process.

2
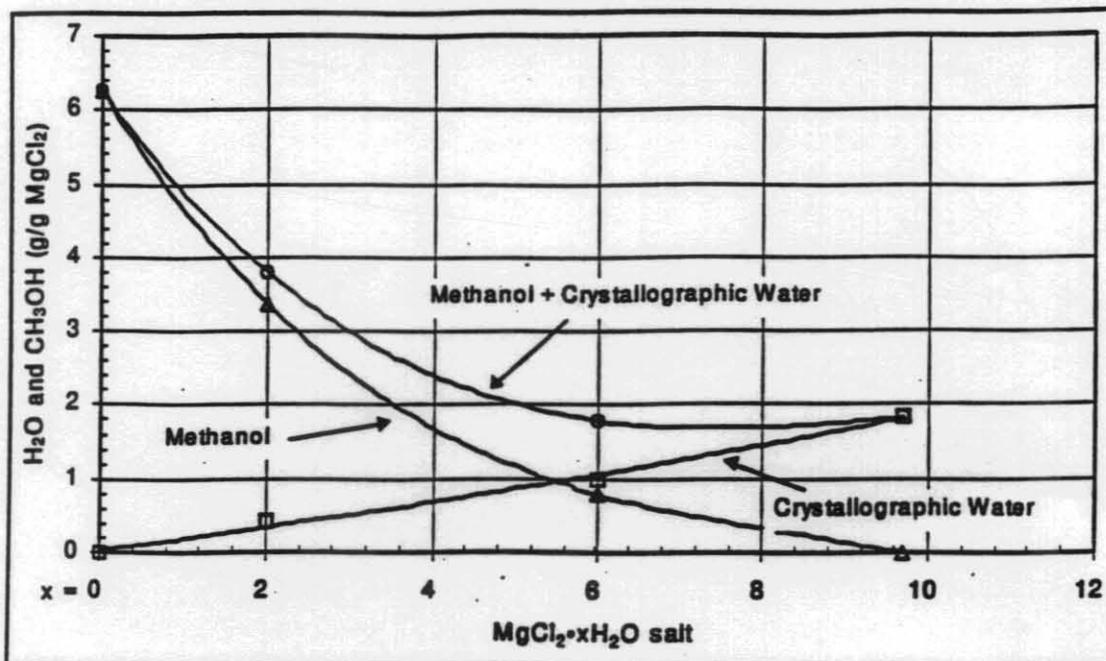
Figure 2-1. Amount of Methanol Required to Dissolve $MgCl_2$ as a Function of its Degree of Hydration
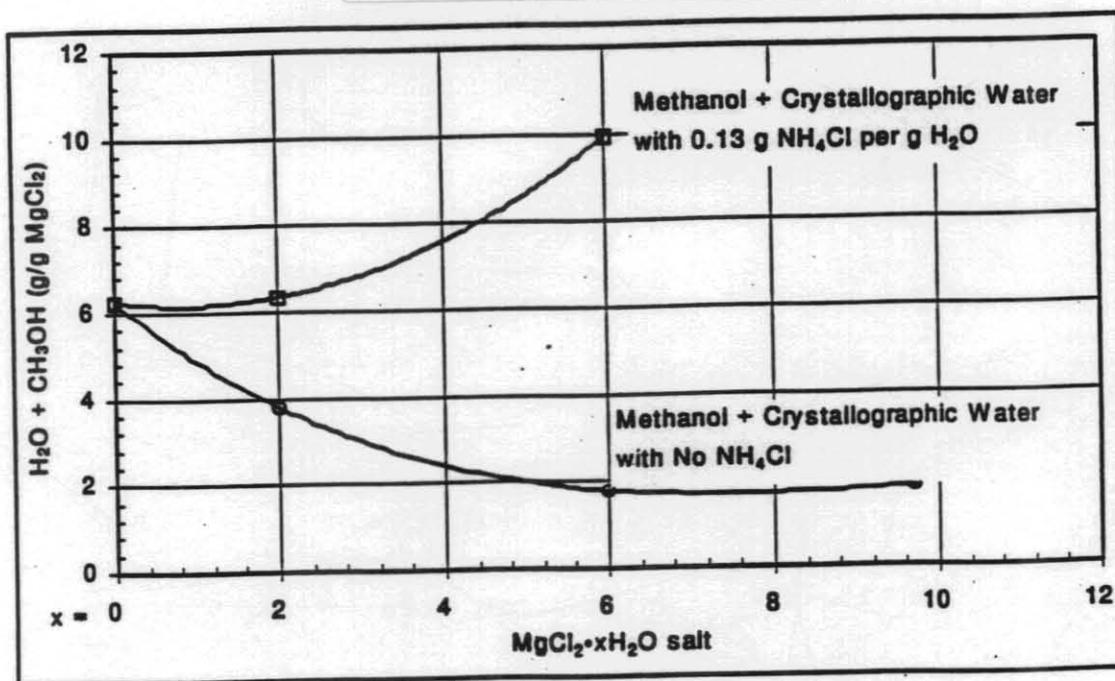
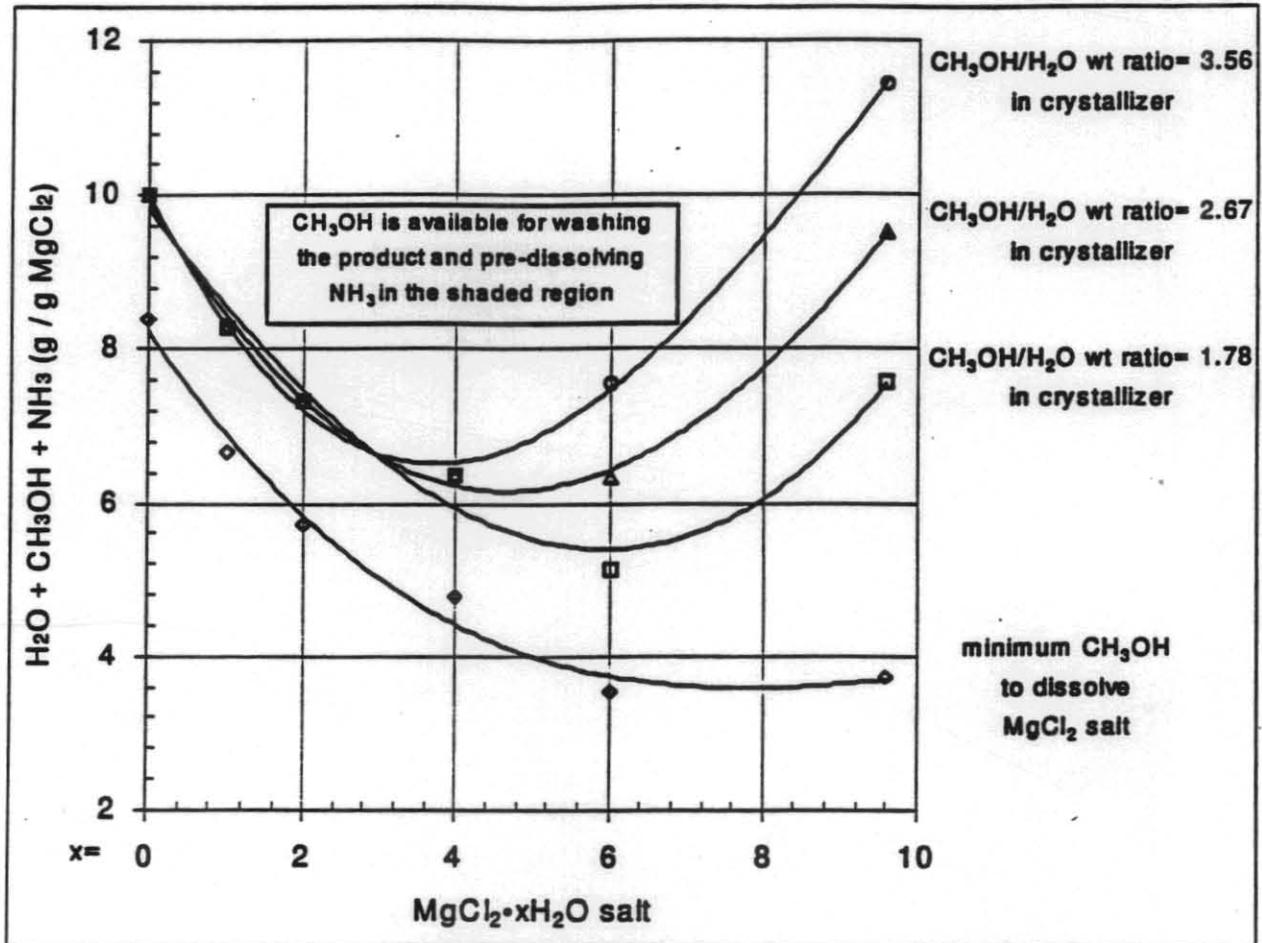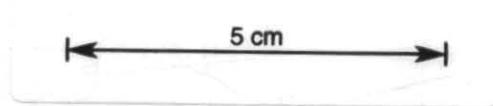

Figure 2-2. Effect of NH_4Cl on $MgCl_2$ Solubility

3

Figure 2-3. Total Reactants required for the Crystallization of $MgCl_2 \cdot 6NH_3$.
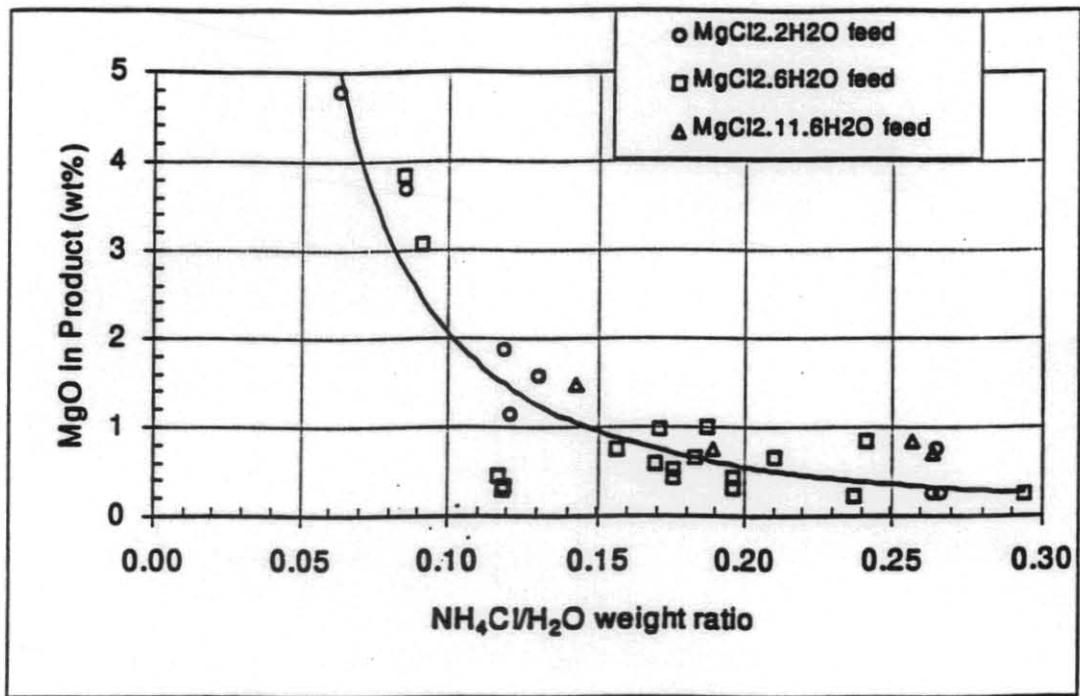
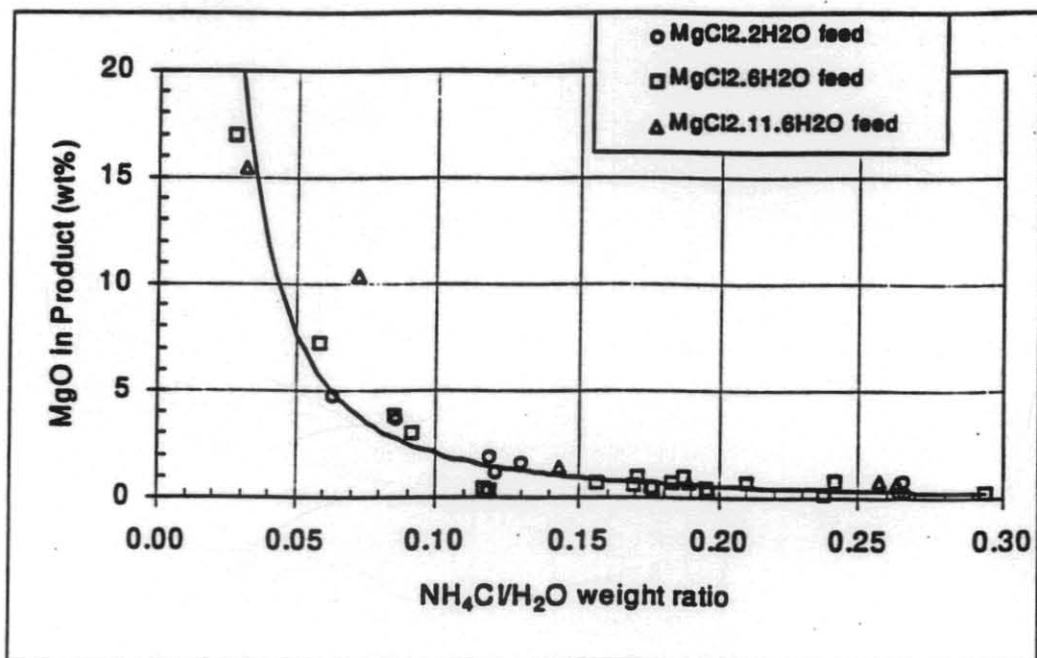**Figure 2-4a.** MgO in Calcined Product as a Function of Ammonium Chloride Concentration

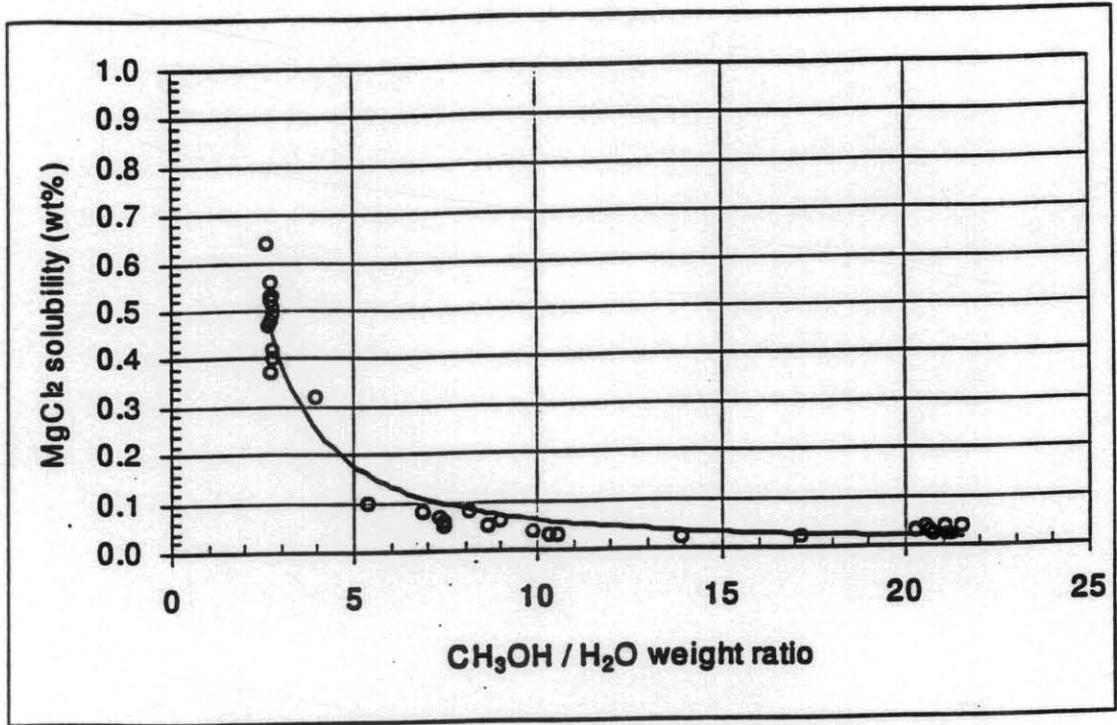**Figure 2-4b.** MgO in Calcined Product as a Function of Ammonium Chloride Concentration (enlarged view of Figure 2-4a)

5

5 cm

Figure 2-5. Effect of Methanol/Water Ratio on $MgCl_2$ Solubility
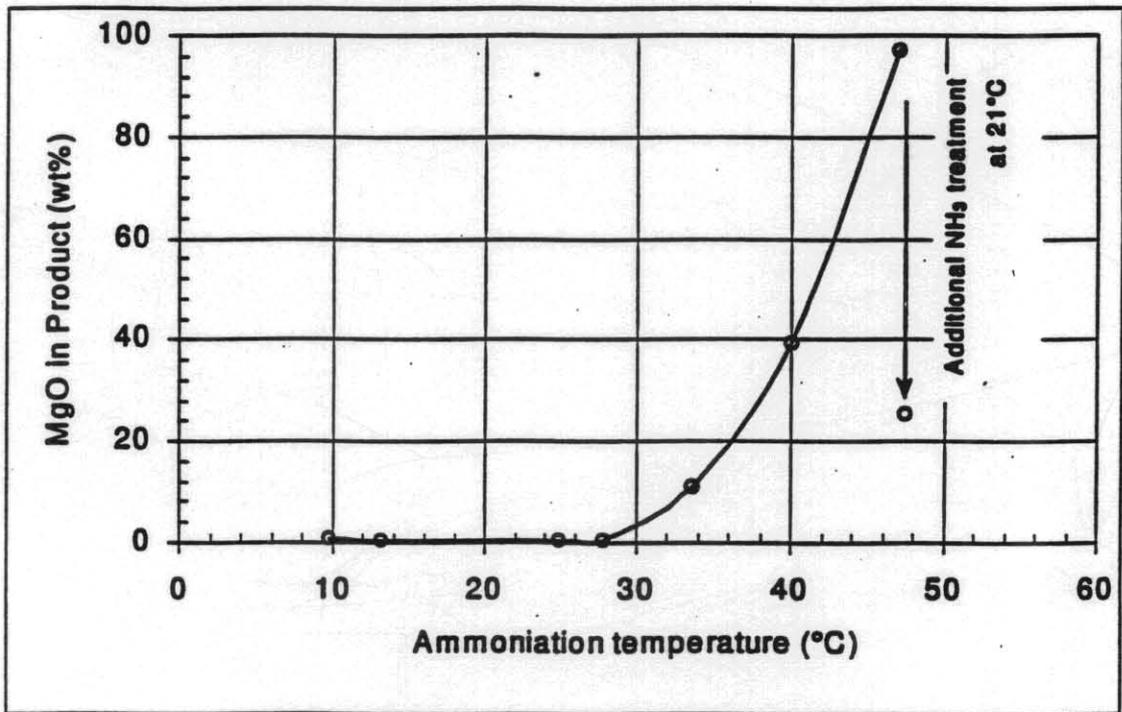
Figure 2-6. Effect of Reaction Temperature on the Product Purity

5 cm

6

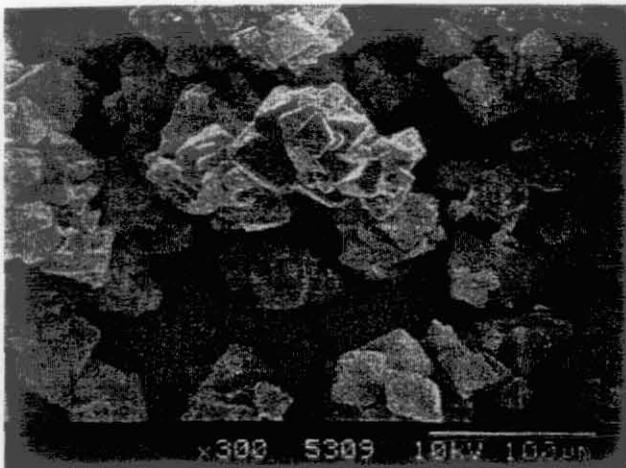**F-3**   **$MgCl_2 \cdot 6NH_3$ CRYSTAL GROWTH AS A FUNCTION OF REACTION TIME FROM ONSET OF PRECIPITATION**
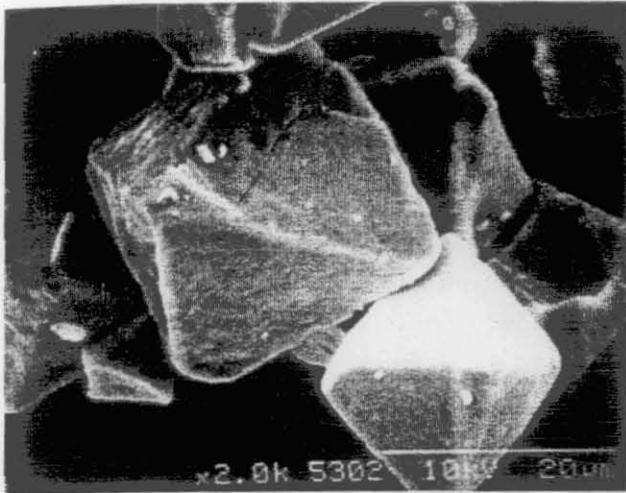
MT32019 $MgCl_2 \cdot 6NH_3$ after 2 min   MT32111 $MgCl_2 \cdot 6NH_3$ after 37 min
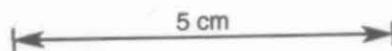
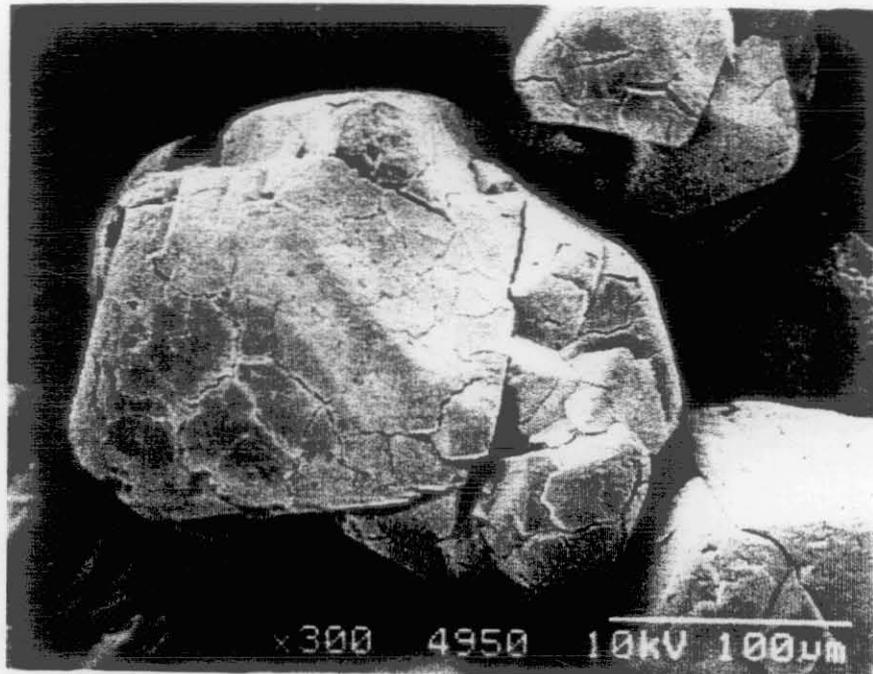MT32105 $MgCl_2 \cdot 6NH_3$ after 8 min   MT32114 $MgCl_2 \cdot 6NH_3$ after 57 min

|← ——— 5 cm ——— →|

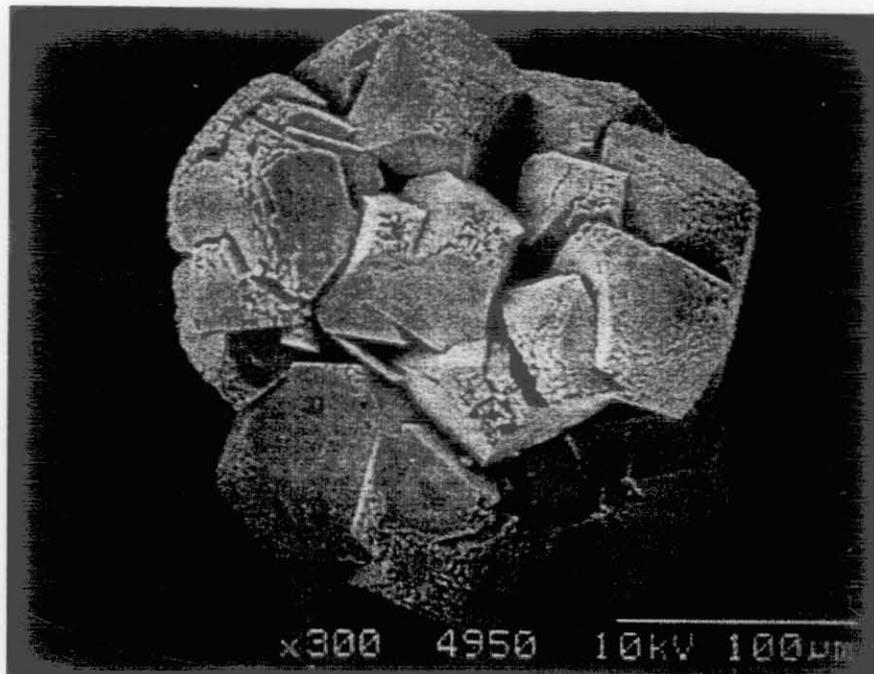## F-4   OTHER $MgCl_2 \cdot 6NH_3$ CRYSTAL MORPHOLOGIES AFTER 60 MIN. REACTION TIME

MT31981 $MgCl_2 \cdot 6NH_3$
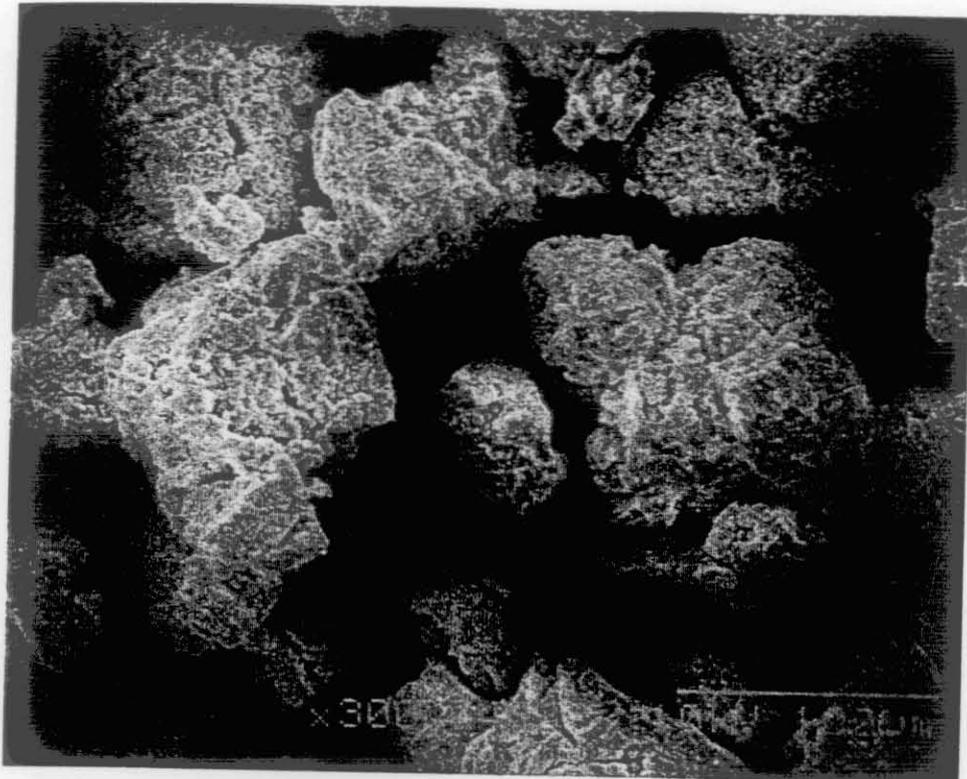

MT31979 $MgCl_2 \cdot 6NH_3$

Alcan International Limited   Alcan Dehydration Technology

ALCAN

F-5   ANHYDROUS MgCl₂: PREPARED FROM MgCl₂·6NH₃ CALCINED AT 600°C

Anhydrous MgCl₂

|←――――――― 5 cm ―――――――→|