

CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

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September 2nd, 1942.

REPORT

of the

ORE DRESSING AND METALLURGICAL LABORATORIES.

Investigation No. 1289.

The Investigation of a Process for Production of  
Magnesium Chloride from Asbestos Waste Rock.

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PART ONE.

Origin of Request and Purpose of Investigation:

A request was presented to the Deputy Minister of Mines and Resources, Ottawa, Ontario, by Col. T. W. MacDowell, V. C., of Westmount, Quebec, for an investigation into the feasibility of a process suggested by Mr. H. G. Wildman, Westmount, Quebec, for the production of magnesium chloride from asbestos waste rock, the said product to be suitable for the manufacture of metallic magnesium.

This report described the laboratory experiments, the procedure employed, and the results obtained. It suggests

(Origin of Request and Purpose of Investigation, cont'd) -

a flow-sheet for the production of a magnesium chloride solution which will furnish a cell feed suitable for use in the fused-electrolyte process for metallic magnesium.

The purpose of the investigation has been confined solely to determining the simplest form of flow-sheet to produce magnesium chloride from pulverized rock, and to present data on this step which might assist in arriving at an estimate of the economic value of this process.

In presenting the matter for investigation, Colonel MacDowell stated that the Shawinigan Chemicals Limited were interested in this process and would be agreeable to cooperate in bringing the investigation to a successful conclusion. To this end they retained Professor J. U. MacEwan, of McGill University, Montreal, Quebec, to act as consultant on the experimental work and assist in the investigation.

Professor MacEwan has periodically visited the laboratory, has kept in touch with the progress made, and has discussed various aspects of investigational procedure.

Acknowledgement is here made of Professor MacEwan's good services and counsel in furthering this investigation.

History:

The Asbestos Industry, centred in the Eastern Townships, Quebec Province, discards daily at least 10,000 tons of waste rock from the production of asbestos. This rock, referred to as "asbestos waste rock," is essentially serpentine with which are associated minerals containing ferric iron, ferrous iron, aluminium, chromium, and nickel. Varying amounts of asbestos fibre remains in the rock. Pure serpentine contains 43.0 per cent magnesium oxide. Samples of waste rock examined in connection with this investigation contained from 34 to 42 per cent magnesium oxide. The impurities also varied considerably.

Mr. H. G. Wildman, of Westmount, Quebec, has had under consideration for some years a plan for the industrial utilization of the asbestos waste rock and proposed using the waste rock as a source of metallic magnesium and magnesium salts and recovering a purified silica and certain base metal products.

Colonel T. W. MacDowell, of Westmount, Quebec, became interested in the industrial possibilities of Wildman's work. In 1941, at his request, this Division of the Department of Mines and Resources made a small-scale laboratory investigation of the chemical reactions involved in the proposed method of leaching the rock and purifying the solution. In general, Wildman's claims regarding leaching and purification were substantiated.

Wildman's Proposed Process:

In brief, the process, as proposed by Wildman, comprised the following steps: Milling the waste rock to reduce the content of iron and other impurities, grinding

(Wildman's Proposed Process, cont'd) -

the milled product to 60 mesh or finer, leaching this in hydrochloric acid, separating the leach liquor from the residue, oxidizing the liquor by chlorine gas from the electrolytic cell or by ~~other~~ suitable means, precipitating the impurities other than nickel by the addition of magnesium oxide made from previously purified magnesium chloride solution, removing the precipitated impurities by filtration, precipitating the nickel by the addition of sodium sulphide and recovering the solution by filtration. The resulting magnesium chloride solution was said to be of a sufficient degree of purity to be processed for making cell feed for the electrolytic production of magnesium. Plants for the manufacture of hydrochloric acid, for evaporating the magnesium chloride solution, and for electrolyzing the fused magnesium chloride, were included in the process. Provision for producing the magnesium oxide and processing by-products was also included.

Other Similar Processes:

Processes based on the acid decomposition of serpentine or similar magnesium silicates have been ~~proposed~~ for the production of magnesium salts and the recovery of one or more by-products (such as ~~activated~~ silica or nickel). Technical literature states that magnesium salts are at present produced by methods using the acid ~~decomposition~~ of olivine as the initial step and that the possibility of extending this process to the commercial production of metallic magnesium is being ~~investigated~~.

The information published regarding these processes is rather meagre, being limited almost entirely to patent literature or to reports of a semi-confidential nature.

Results of Investigation:

As conducted in the laboratory, the investigation shows that a magnesium chloride solution of a purity suitable to yield cell feed for fused-electrolyte production of magnesium metal can be produced from asbestos waste rock.

The different reactions involved in the leaching and purification are comparatively simple and easily controlled. Standard equipment is indicated, such as acid-proof tanks and stirrers, with thickeners, filters, etc., of conventional design.

The process as developed may be briefly described as follows:

1. Grinding the waste rock to minus 35 mesh and tabling to remove as much as possible of the iron and spinel minerals.
2. Leaching the ground rock in 18 per cent (approximately 12° Be) hydrochloric acid at a temperature around 70° C. until the acidity is reduced to 0.3 per cent or less. A 25 per cent excess of waste rock is necessary to accomplish this in minimum time.
3. Diluting the pulp, on completion of leaching, with sufficient water to give a liquor containing about 10 per cent magnesium chloride. Stronger solutions (20 per cent  $MgCl_2$ ) have shown a tendency to form oxychloride and form a jelly-like solution. The exact point of this reaction has not been determined but the 10 per cent magnesium chloride solution was arbitrarily selected as being safe. Chloride retention in the precipitate has generally been found to be higher with increased magnesium chloride concentration.
4. Precipitating the dissolved impurities, such as iron, alumina and nickel, by the addition of freshly calcined brucite or magnesium oxide to the pulp at 50° - 70° C. until a pH of about 7.0 - 7.5 is obtained.
5. Filtering the pulp to remove solids, washing, and then clarifying the filtrate.

The above procedure differs from Wildman's suggested process in the following respects:

(Continued on next page)

(Results of Investigation, cont'd) -

- (a) Coarser grinding is employed, as a difficult filtration step is improved at slight expense of leaching time.
- (b) Leaching and purification are carried out without intermediate filtration.
- (c) Oxidation of iron is not necessary prior to precipitation of impurities.
- (d) One precipitant only, namely prepared brucite (MgO), or other form of magnesium oxide, is used to completely precipitate iron, alumina, and nickel.
- (e) One main filtration only is required, with subsequent clarification to produce a clear and pure magnesium chloride solution.

By the above procedure the hydrochloric acid losses are confined to two points, excepting losses incidental to leaks, spills, etc., namely, (1) loss by volatilization during leaching, and (2) chlorides contained in the filter solids. No tests were made in the laboratory investigation with respect to volatilization losses as these can be minimized in designing equipment by use of hoods for recovering losses. Laboratory tests have shown that by proper technique, acid or chloride losses in the filter cake can be controlled and kept low. Wash solutions from filtration will naturally be used in making up acid leach liquor or in dilution of liquor prior to precipitation of impurities.

The magnesium chloride produced by this method has a purity of the following order, based on metallic magnesium:

Total iron	-	Less than 0.002 per cent.
Nickel	-	" " 0.004 "
Chromium	-	" " 0.0004 "
Silicon	-	" " 0.008 "
Calcium	-	Faint trace.
Aluminium	-	No satisfactory test available but content very low.

No other detrimental impurities were found.

(Continued on next page)



(Results of Investigation, cont'd) -

The second part of this report describes in detail the various laboratory tests and results, and discusses several points respecting technique and other matters of importance.

Test Data and Flow-Sheet:

From large-scale tests the following example is presented as typical of the results that may be expected following the procedure outlined:

A 75-pound charge of waste rock\* (36 per cent MgO), ground to pass 35-mesh screen, was leached (agitated) with 123 pounds 20° Be hydrochloric acid and 93 pounds of water for 3 hours at around 70° C. The acidity reached 0.3 per cent hydrogen chloride in this time. The pulp was diluted with 200 pounds water (70° C.) and 8.5 pounds of freshly calcined brucite (or 5.0 pound C.P. MgO) were added in small portions over a period of 15 minutes.

The pulp solution, with a pH of 7.1, was fed to a Hardinge-type superthickener, the overflow going direct to a clarifier and the underflow to a filter. The underflow comprised about 50 per cent solids and the filter rate was approximately 800 pounds of solution per hour.

The filter cake was given a water wash (A) with 65 pounds water (60° C.) and then discharged and repulped in 50 pounds water (60° C.) and refiltered (B) with a single water wash (C) of 36 pounds. The wet cake weighed 74 pounds and contained 37 per cent water (dried at 110° C.).

The total chloride content of the cake (sample taken before drying) was 0.27 per cent dry hydrogen chloride (HCl). The magnesium chloride content of the liquor was 9.10 per cent

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\* See analysis in section on large-scale tests (Page 30).

(Test Data and Flow-Sheet, cont'd) -

MgCl<sub>2</sub> (anhydrous) and the weight of the recovered liquor was 480 pounds.

The filter washes were as follows:

1st Wash A <sup>⊕</sup>	-	65	pounds	9.1	per cent	MgCl <sub>2</sub> .
Repulp Filtrate B and 2nd Wash C	-	86	"	1.8	"	"

In the laboratory equipment set up some loss of filtrate solutions was unavoidable, so that the recovered magnesium chloride is somewhat lower than would obtain in correct alignment of equipment.

The wash waters will, of course, be returned as dilution water or in acid make-up, so that no chloride loss is involved there. The total chloride loss is therefore confined to that contained in the washed filter cake and in volatilization losses during leaching. The latter can be minimized in plant operation by proper design.

The chloride loss in filter cake, therefore, would be  $\frac{0.27}{100} \times 74 \approx 0.20$  pounds dry hydrogen chloride (HCl) after the above washing procedure.

Eliminating repulping, and washing only on the filter, the hydrogen chloride loss would be in the neighbourhood of one to two per cent.

PLANT OPERATION DATA:

Leaching Plant.

Solids: Serpentine-Asbestos Rock. S.G., 2.3.  
Solution: HCl, 18 per cent solution.  
Temperature: 70°C.  
Leach density: 24 per cent solids (3.1:1).  
Time: 3 hrs. (max.).  
Precipitation density: 14 per cent solids (6.1:1).  
Time: 1 hour.  
Precipitant: Magnesia (calcined brucite).

<sup>⊕</sup> Original filtrate and first wash were combined owing to the type of filter used.

(Plant Operation Data, cont'd) -

Thickening-Filtration-Clarification Plant.

Thickening:

Feed - 14 per cent solids (6.1:1).  
Disch. - 50 " " (1:1).  
Settling rate, - 0.78 ft./hr.  
Area required/ton/24 hrs. - 9.0 sq. ft.

Filtration:

	Feed - 50 per cent solids.	
Approximate )	Plate and Frame - 150 lb./sq.ft./24 hrs. (35 p.s.i.)	)
filtering )	Oliver - 160 " " " (25 " Vac.)	)
rates. )	Dorrco - 250 " " " (22 " Vac.)	)

Clarification:

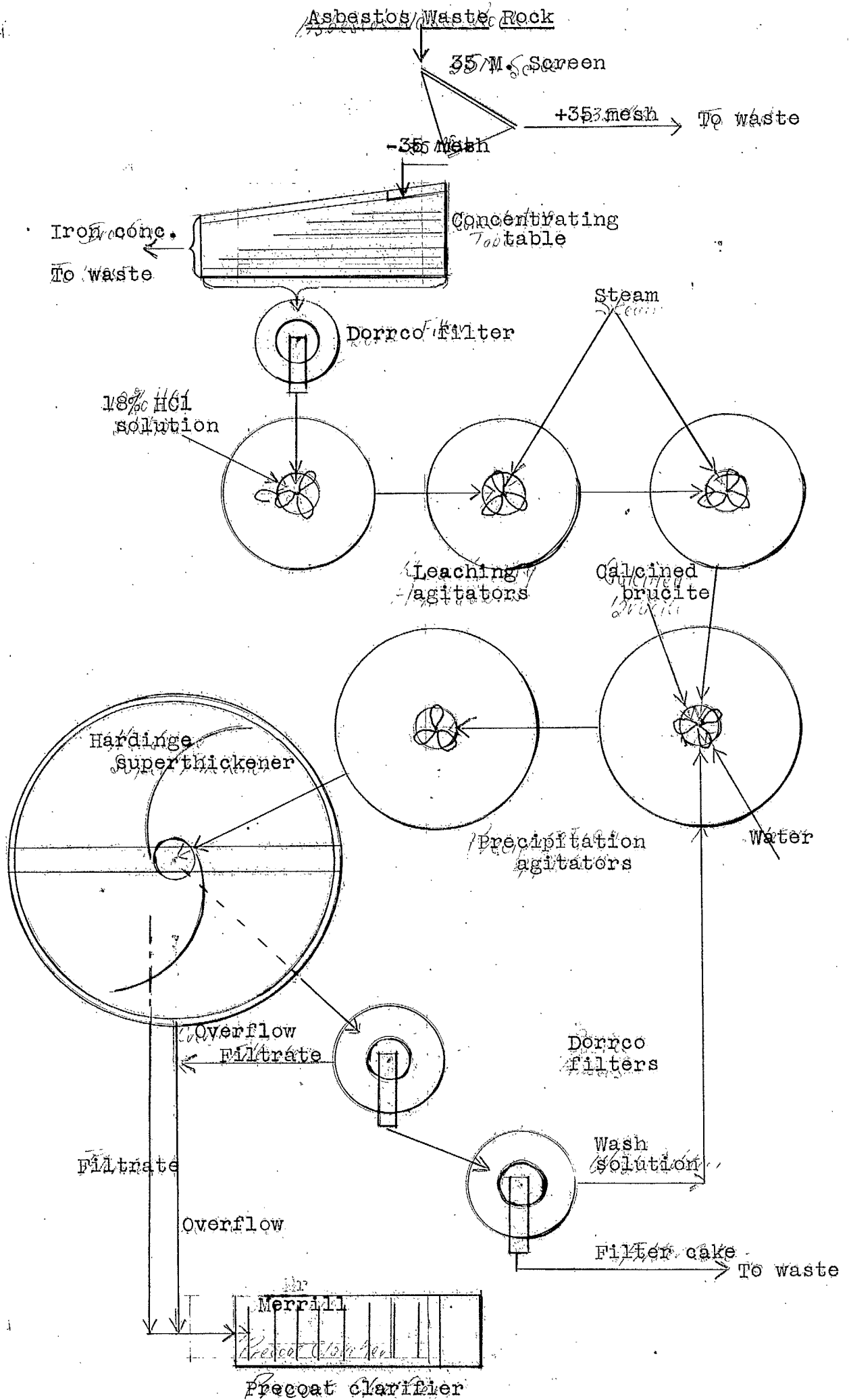
Feed - Filtrate + thickener overflow.  
Rate - 1600 lb./sq.ft./24 hrs.

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Complete details of laboratory small-scale  
and large-scale tests will be found in  
PART TWO of this report.

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PROPOSED FLOW SHEET



PART TWO.

Laboratory Investigation.

Small Scale.

Shipment:

A shipment of 2,020 pounds of asbestos waste rock was received from the Asbestos Corporation, Thetford Mines, Quebec, on April 3rd, 1942, through the cooperation of Professor J. U. MacEwan. The shipment consisted of four lots, of about 500 pounds each, from four different mines in the Thetford district and was said to be representative of the waste rock of this district. The four lots were quite similar in chemical analysis. The lots were tabled separately and the composite table tailing used in the leaching tests.

A small shipment, of about 20 pounds, was also received. This consisted of four lots of about 5 pounds each cut from the above lots previous to shipment.

Sampling and Analysis:

The composite tailing was sampled and analysed.

	<u>Per cent</u>
MgO	38.63
SiO <sub>2</sub>	38.54
Al <sub>2</sub> O <sub>3</sub>	1.08
Cr <sub>2</sub> O <sub>3</sub>	0.28
Ni	0.23
CaO	Trace
Fe <sub>2</sub> O <sub>3</sub>	3.44
FeO	1.72
Metallic Fe	0.65
Total Fe	4.33
H <sub>2</sub> O	Not determined.

Part of the composite tailing was ground to different degrees of fineness. The screened sizes of the three products were:

(Continued on next page)

(Sampling and Analysis, cont'd) -

<u>Mesh</u>	<u>Coarse composite tailing, per cent</u>	<u>Fine composite tailing, per cent</u>	
		<u>-35 mesh</u>	<u>-48 mesh</u>
+ 10	0.6		
- 10+ 14	1.9		
- 14+ 20	17.5		
- 20+ 28	19.0		
- 28+ 35	17.2	0.2	
- 35+ 48	14.0	14.0	1.4
- 48+ 65	10.5	20.6	16.3
- 65+100	7.4	16.3	20.7
-100+150	5.4	14.5	20.6
-150+200	3.5	10.5	13.1
-200	3.0	23.9	27.9
	100.0	100.0	100.0

LABORATORY PROCEDURE:

A large number of tests of a preliminary nature were made on these products to find the effect of different types of feed, and to determine the acid strength, the temperature, and the leaching time required to obtain practical decomposition. Only a few tests were made on the 20-pound lot as received and on the coarse composite tailings, the other tests being made on the -35 and the -48 mesh products.

Based on the results of these tests, the following general procedure was adopted:

The waste rock was tumbled to remove spinels and the table tailing was ground to minus 35 mesh. In order to obtain complete acid consumption an excess of feed (usually 25 per cent) was used.

The required amount of 18 per cent hydrochloric acid was heated to 40° C., the feed added, the pulp agitated to keep the solids in suspension, and the heat source regulated to keep the temperature of the pulp at 50-70° C.

Samples of the solution were removed from time to time

(Laboratory Procedure, cont'd) -

for the determination of the residual free acid.

When the residual free acid was reduced to at least 2 per cent of the total acid originally taken, the leaching was discontinued.

The pulp was filtered and the residue washed three times with a measured amount of water. As a rule the first wash was added directly to the leach solution. Each wash was about 25 to 30 per cent by weight of the leach solution.

The leach solution and the washes were analysed and the residue was examined for chlorides.

The 250- and 500-gram lots were leached in beakers, the 2½-kilo. lots were leached in stoneware jars.

Typical Test Results Obtained:

The following tests are typical of results obtained when this routine was followed. In Test No. 6 the first wash is not included in the extraction solution.

Tests.

Test No.	Weights taken: Rock, grams	: 18% HCl, grams	Temp., degrees C.	Leaching: time, hours	Acid con- sumption, per cent	Final acid- ity of pulp, per cent
4	250	776	50-70	4	98.6	0.25
6	250	776	"	4	98.4	0.29
8	500	1552	"	4	98.4	0.29
12	500	1552	"	4	98.2	0.33
13	2500	7760	"	4	98.0	0.35
14	2500	7760	"	4	98.0	0.35

Leach Solutions.

Test No.	Weight of: solution, grams	Specific: gravity	MgCl <sub>2</sub> , per cent	Iron, per cent	Ferric: Ferrous	Al	Ni	CaO	Cr
4	985	1.160	16.23	0.32	0.31	0.12	0.04	Tr.	Trace
6	820	1.189	17.21	0.36	0.34	0.15	0.05	"	"
8	2,007	1.159	16.12	0.29	0.30	0.13	0.05	"	"
12	1,998	1.158	15.95	0.28	0.31	0.13	0.04	"	"
13	10,112	1.150	15.82	0.30	0.29	0.12	0.04	"	"
14	10,060	1.153	15.63	0.32	0.30	0.14	0.05	"	"

(Continued on next page)

(Laboratory Procedure, cont'd) -

Washes.

- No. 1. - When kept separate and analysed, 6 to 8 per cent  $MgCl_2$ .
- No. 2. - Less than 0.2 per cent  $MgCl_2$ .
- No. 3. - Mere trace  $MgCl_2$ .

The filtration rate was about 100 grams solution per minute when using a Buchner-type filtering funnel of a size to give a bed of residue  $\frac{5}{4}$  inch thick.

Residues.					
Test No.	Reduction in weight, per cent	Chloride content as HCl, per cent	Per cent of total acid in residue (as chlorides).		
4	37.5	0.07	0.078	:	:
6	37.2	0.05	0.056	:	:
8	37.6	0.06	0.069	:	:
12	37.4	0.04	0.045	:	:

In Tests Nos. 13 and 14 a small laboratory-size filter press was used but trouble was experienced in washing the cake and some of the cake was lost.

PURIFICATION OF THE LEACH LIQUOR:

The metallic chloride content of the leach liquor obtained by the leaching practice described is approximately 87 per cent  $MgCl_2$  and 13 per cent chlorides of iron, aluminium, chromium and nickel, considered as the anhydrous chlorides in each case. This represents a metal content of approximately 83.4 per cent Mg and 16.6 per cent metallic impurities.

Very few data have been published on the nature or limits of the impurities permissible in dehydrated  $MgCl_2$  used as cell feed in the electrolytic production of magnesium. Gann states (Ind. and Engl Chemistry, Vol. 22, No. 7, July 1930)



(Purification of the Leach Liquor, cont'd) -

that by using cell feed containing less than 0.01 per cent heavy metal impurities capable of affecting the quality of the metallic magnesium, metal of 99.9 to 99.95 per cent purity was produced and that the impurities consisted of silicon, iron, aluminium, and manganese.

A  $MgCl_2$  solution which will give anhydrous  $MgCl_2$  well within this range of purity can be obtained by purifying the leach liquor resulting from the acid decomposition of asbestos waste rock. The purification is brought about by the use of  $MgO$  (or its equivalent) under proper conditions. The  $MgO$  neutralizes the residual acid and decomposes the chlorides of iron, aluminium, chromium and nickel to form the hydroxides of these metals and  $MgCl_2$ . When the precipitated metallic hydroxides are removed by filtration the purified  $MgCl_2$  solution is obtained. By this method of purification all the metallic impurities present in the leach liquor are removed in one step and the  $HCl$  which had reacted during the leaching period in forming the chlorides of these metals is recovered and is represented in the purified solution by  $MgCl_2$ .

It is obvious that the acid in the leach step should be utilized to the fullest extent, as residual acid will consume precipitant reagents. It is also obvious that the higher the content of impurities, namely iron oxides, alumina, etc., the greater the amount of precipitant to be added.

The amount of a precipitant to be added can be estimated if the residual acid and the amount of each impurity present as a metallic chloride in the leach solution are known. It was found simpler in all cases to add the precipitant gradually over a period of about 30 minutes until the solution has attained a pH of at least 7.0 and then agitate for an additional

(Purification of the Leach Liquor, cont'd) -

30 minutes, or longer if necessary, before filtering. The average leach liquor made from this feed requires 13.0 grams MgO per kilogram solution; this includes an excess of 25 per cent above the estimated requirement.

When a precipitant other than MgO was used in treating leach liquors of a rather high  $MgCl_2$  (e.g. 16 or 17 per cent  $MgCl_2$ ), it was not found possible to consistently obtain complete purification even though excess precipitant was used and the treatment time was lengthened.

Results indicate that the tendency for chloride retention by the metallic hydroxide precipitate is greater when precipitation takes place in a solution high in  $MgCl_2$  than when it takes place in a more dilute solution. For these reasons the leach liquor was usually diluted with an equal weight of water before purification. This gave a purified solution containing about 10 per cent  $MgCl_2$ .

During the addition of the MgO the pH of the solution was measured by means of a pH meter using a glass electrode. No attempt was made to find the pH at which each hydroxide formed. Britton states (Hydrogen Ions, p. 278) that the hydrogen-ion concentrations at which the hydroxides are precipitated from dilute solutions are:

Mg	-	10.5
Ni	-	6.7
Fe <sup>II</sup>	-	5.5
Cr	-	5.3
Al	-	4.2
Fe <sup>III</sup>	-	2(?)

Qualitative tests indicated that the Fe<sup>III</sup>, Cr, Fe<sup>II</sup> and Ni were precipitated in this order, but the exact pH was not determined.

(Continued on next page)

(Purification of the Leach Liquor, cont'd) -

Several precipitants were tested. In each case the precipitate formed is voluminous, rather gelatinous in nature, and has a tendency to retain chlorides. In selecting a precipitant its efficiency in bringing about complete precipitation, the filterability of the precipitates formed, the amount of chloride retention, and the cost of the precipitant are factors to be considered.

The following precipitants were used:

- (1) Additional waste rock.
- (2) Calcined waste rock.
- (3) Prepared brucite made by calcining and washing brucite ore to reduce the CaO to a low percentage. Different lots of prepared brucite at different degrees of hydration and of different screen sizes were used.
- (4) Basic magnesium carbonate, made from previously purified magnesium chloride solution by precipitation with  $\text{Na}_2\text{CO}_3$ .
- (5) MgO, made by calcining the basic magnesium carbonate.
- (6)  $\text{Mg}(\text{OH})_2$ , made by hydrating the MgO.

Each of these precipitants required a somewhat different procedure.

#### Precipitation Procedures.

##### (1) Additional Waste Rock.

It was not found possible to obtain purification by treating the unoxidized leach liquor with additional waste rock. Part of the ferric iron was precipitated, the other impurities remained in solution.

The diluted leach solution was oxidized by means of chlorine gas, waste rock was added, the pulp was agitated at 50-70° F. and treated with chlorine gas simultaneously. When an amount of ore equal in weight to that used in producing the leach liquor was added, a four-hour treatment resulted in the precipitation of practically all of the iron. The nickel was

(Precipitation Procedures, cont'd) -

left in solution.

(2) Calcined Waste Rock.

The coarse waste rock was calcined for two hours at 600° C., then ground to -35 mesh.

The diluted leach liquor was agitated with various different amounts of the calcined waste rock at 50-70° C. When an amount equivalent to 60 per cent of the waste rock used in making the solution was added, agitating for two hours gave satisfactory purification. The filtration rate was fair, the chloride retention low.

No further tests were made on the use of the waste rock for purification purposes as it was thought more suitable precipitants were available.

Brucite, Magnesium Carbonate, Magnesium Oxide -

Several preliminary tests were made using the above precipitants. The following general procedure was indicated:

A weighed amount of the leach solution (usually 2 kilograms) was diluted with an equal weight of water. The solution was agitated and the precipitant added gradually over a period of about 30 minutes until the solution attained a pH of at least 7.0. The agitation was continued for another 30 minutes or longer and was carried out at 50-70° C. (except when MgO was used). When the required addition of precipitant had been determined in this way the same effect was obtained in subsequent tests by adding the total amount of the precipitant at one time.

Tests were also made in purifying the undiluted leach liquor.

After the required amount of precipitant had been added samples of the solution were withdrawn and tested qualitatively for total iron and nickel. Though the ferric

(Precipitation Procedures, cont'd) -

iron precipitates first (at a pH of about 2), it is the most difficult of the impurities to remove completely. When these tests indicated satisfactory purification of the solution the pulp was filtered. A second filtration was always necessary to remove the semi-colloidal particles. The residue was washed three times with known amounts of water. As a rule the first wash was added directly to the purified solution. The purified solution was analysed for its  $MgCl_2$  content and for impurities. Each wash was analysed for its  $MgCl_2$  content. The residue was air dried, sampled, and analysed for retained chlorides.

The  $MgCl_2$  content of the purified solution was estimated from the specific gravity of the solution. This method was found to give results in fair agreement with those obtained by chemical analysis.

### (3) Prepared Brucite.

Freshly calcined prepared brucite ground to minus 200 mesh, minus 100 mesh, or coarser was used in most of the tests.

The minus 200 mesh brucite had practically the same precipitating value as artificial  $MgO$ ; the minus 100 mesh material has a somewhat lower precipitating value; the coarser sizes have decidedly lower precipitating value.

The finer the mesh of the precipitant used the slower the filtration rate of the precipitate formed. When minus 100 mesh is used the filtration rate is fair. This was taken as the most serviceable size for these tests on the filtered leach liquor.

Partly hydrated prepared brucite containing up to 100 per cent  $H_2O$  was found satisfactory. However, if a large excess of this material is used or if it is added to a solution of a

(Precipitation Procedures, cont'd) -

high  $MgCl_2$  content a viscous unfilterable mass is formed.

The action of prepared brucite is too slow at room temperature to be considered practical. At 50-70° C. satisfactory purification is obtained by treating for 1 hour. When purifying a diluted solution, a pH of 7.5-8.5 was usually obtained. Satisfactory purification of the undiluted solution was not obtained with brucite.

(4) Basic Magnesium Carbonate.

The basic carbonate contained 45.4 per cent  $MgO$ , specific gravity 2.569.

It was found necessary to use a greater excess of the carbonate than that estimated from its  $MgO$  content. The highest pH obtained was 7.0. Agitation at room temperature was not satisfactory. Agitation for 3 hours at 50-70° C. gave satisfactory purification when precipitating a diluted solution. The filtration is rather slow, the chloride retention is the lowest for any of the reagents used.

An undiluted solution could not be successfully purified. The addition of a large excess of precipitant and prolonged agitation at 50-70° C. did not increase the pH beyond 6.5.

(5) Magnesium Oxide.

Magnesium oxide, made from the basic carbonate, and a commercial sample of heavy oxide were used. No essential difference was found in their behaviour.

Agitating with  $MgO$  at room temperature or at more elevated temperatures gave satisfactory purification when treating either a diluted or an undiluted solution in one hour. A pH of 7.5-8.5 was usually obtained. When an alkalinity greater than this is obtained in treating the diluted solution, there is

(Precipitation Procedures, cont'd) -

a tendency for a magnesium precipitate (presumably an oxychloride) to form after filtration. With an undiluted solution the same tendency is exhibited at alkalinities lower than 8. This tendency can be corrected by the addition of a small amount of HCl. From the standpoint of precipitation only, MgO is the most efficient of the different precipitants tested. The filtration is rather slow; the chloride retention is higher than that obtained with the basic carbonate.

Samples of light MgO used gave similar results except that the filtration rate was slower.

(5) Magnesium Hydroxide.

Acted very similarly to MgO; no detailed study was made.

Analysis of the Purified Solutions.

No satisfactory chemical methods were found for the quantitative determination of the metallic impurities in the purified solution. Except in the case of chromium the relatively high concentration of  $MgCl_2$  interfered to a certain extent in the application of the methods usually found satisfactory in determining traces of these elements.

By using a  $MgCl_2$  solution made from C.P.  $MgCl_2 \cdot 6H_2O$  it was found that the following amounts of added substances could be detected. No attempt was made to determine the minimum amount detectable. The element is reported in per cent based on the Mg present.

		<u>Per cent</u>
Fe	-	0.002
Ni	-	0.004
Cr	-	0.0004
Si	-	0.008
Al	-	No suitable method found.

When purified solutions were found to contain Fe and

(Analysis of the Purified Solutions, cont'd) -

Ni in amounts greater than this the purification was considered unsatisfactory. In all solutions tested it was found that, if the Fe and Ni were within the limits, the purification was satisfactory.

Qualitative spectrographic tests indicated only traces of these elements.

Careful clarification previous to analysis is necessary.

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Other Precipitants.

Precipitants other than those shown were not tested but it is conceivable that sodium carbonate or sodium hydroxide could be used provided the amount added were not in excess of that required as addition agent in the subsequent electrolysis of fused  $MgCl_2$ .

In using sodium carbonate it might be said that this operation would require to be conducted in a manner to avoid generation of excessive  $CO_2$ , as this would tend to form bicarbonates of the metals, with resulting greater impurities in the  $MgCl_2$  solution.

LEACHING AND PURIFICATION WITHOUT AN INTERVENING FILTRATION:

In these tests the leaching was carried out in the usual way. When the acid consumption had reached 98 per cent or more the pulp was diluted so as to give a  $MgCl_2$  content of about 10 per cent, the precipitant was added and the purification carried out in the usual manner.

When the brucite or  $MgO$  was used as precipitant this method gave good results, a pH of 7-8 was obtained. The filtration rate was fair.



(Leaching and Purification without an Intervening Filtration, cont'd) -

Satisfactory purification was not obtained when basic carbonate was used even in excess. A pH of 7.0 was indicated but the solution contained an appreciable amount of iron.

When the rock was leached and the precipitant added without diluting the pulp, satisfactory purification was not obtained with brucite, basic magnesium carbonate or MgO. Excesses of the reagents were used but a sufficiently high degree of alkalinity was not obtained with any of these precipitants.

The following tests are typical of the results obtained in purifying the leach liquor.

The purification was not termed satisfactory if the impurities found exceeded the limits given on page 21.

Test No. :	Precipitant used :	Treatment : time, hours :	Temperature, : degrees Centigrade :	Final : pH :	Purification :
21-c :	Brucite 30 gm.	1	50-70	8.2	Satisfactory
21-d :	30 gm.	1	50-70	8.0	"
21-e :	Basic MgCO <sub>3</sub> 60 gm.	3	50-70	7.0	"
21-h :	60 gm.	3	50-70	7.1	"
21-a :	MgO 6x13 gm.	1	room temp.	8.5	"
21-c :	26 "	1	" "	8.3	"
30-a :	MgO 13 gms.	1	room temp.	7.6	"
30-b :	Basic MgCO <sub>3</sub> 70 gm.	4	50-70	6.5	Unsatisfactory
30-c :	Brucite 40 gm.	2	50-70	6.8	"

21-a - 6 kilos. extraction solution.

30-a - 1 kilo. " "

2 kilos. in other tests.

30-a, 30-b, 30-c, undiluted, other tests diluted with equal weights of water.

Brucite used was freshly calcined minus 100 mesh brucite.

CHLORIDE RETENTION:

When the insoluble residue left after leaching is washed three times with a total weight of water 75-90 per cent that of the leach solution the chloride content of the residue averages 0.2 per cent (stated as 18° Bé HCl).

In precipitating the metallic hydroxides in the filtered solutions various methods of filtering and washing were tried in the different tests. As a rule the precipitate was washed three times using in all 60-75 per cent as much water as the solution being filtered. The first wash was added directly to the purified solution. This method gave a residue containing 4 to 6 per cent chlorides (stated as 18° Bé HCl).

In an attempt to improve on this the hydroxide precipitate after a preliminary wash was dried at 100° C., ground to minus 100 mesh, agitated with water and filtered. This procedure reduced the chlorides retained in the precipitate by about 50 per cent. Such a scheme, however, does not appear attractive from a cost viewpoint.

Later work demonstrated that precipitating the impurities in the leach pulp in presence of the insoluble gangue and filtering and washing, gave more satisfactory results in every way.

The hydroxide precipitate obtained by laboratory practice has a very high moisture content. This may account for its rather high chloride content.

The table below gives data obtained on purifying the solutions under different conditions. In Tests Nos. 16-c, 21-d, 21-e, 21-h, 21-a and 21-c the leach solution was diluted to give a purified  $MgCl_2$  solution of 9-12 per cent. In Test 30-a the undiluted leach solution was used. In Tests 23-a and 23-b the unfiltered pulp was diluted to give a

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(Chloride Retention, cont'd) -

purified  $MgCl_2$  solution of 10-11 per cent. It was not found possible to obtain satisfactory purification by treating the undiluted unfiltered pulp.

The column 'Chlorides in Solids' gives the chlorides in the total solids in Tests 23-a and 23-b. In each of the other tests the chlorides found in the hydroxide precipitate only is shown. The last column gives the total chloride retention, namely, gangue insoluble plus hydroxides.

CHLORIDE RETENTION

Test No.	Material treated	Precipitant	$MgCl_2$ in purified solution, grams	$MgCl_2$ in final wash, per cent	Chlorides in solids as 18° Be HCl, per cent	Chlorides in solids as 18° Be HCl, grams
16-c	4K diluted sol.	Brucite	393.4	0.54	2.2	5.4
21-d	4K " "	"	374.2	0.67	3.1	6.8
21-e	2K " "	Basic carb.	186	0.41	0.21	1.47
21-h	4K " "	" "	369	0.32	0.20	2.02
21-a	12K " "	MgO	1146	0.72	2.6	26.5
21-c	4K " "	"	362.3	0.87	2.8	6.2
30-a	1K undiluted solution	MgO	193.4	0.56	2.5	5.7
23-a	Diluted pulp	Brucite	363.5	0.47	1.07	6.7
23-b	" "	"	357.6	0.56	1.25	7.5
31-a	Undiluted pulp	MgO	Unsatisfactory purification.			
31-b	" "	Brucite	"	"	"	"
31-c	" "	Basic carb.	"	"	"	"

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CONCLUSIONS FROM SMALL-SCALE TESTS:

Leaching.

Milling the waste rock previous to leaching to reduce the amount of iron and other impurities conserves the acid and reduces the amount of impurities to be removed in purification of the solution.

Grinding the rock to minus 35 mesh or finer reduces the leaching time. No appreciable difference was found between the leaching time required for minus 35 and minus 48 mesh feed.

Leaching with 18 per cent HCL at 50-70° C. was found to be the most satisfactory procedure. Using minus 48 feed and 18 per cent HCL at 50-70°C. The rates of acid consumption in typical tests are:

In 1 hour leaching	80-84	per cent consumed.
" 2 hours	" 92-94	" "
" 3 "	" 96-97	" "
" 4 "	" 98-98.6	" "

Only a very small increase in acid consumption was obtained by continuing the leaching beyond 4 hours.

The leaching time can be lessened by increasing the temperature. In small-scale work, however, the temperature control is difficult, as a rule the temperature range was 60-65°C.

When the rock was leached with 10 per cent HCL at 50-70° C., 90-92 per cent of the acid was consumed in 6 hours. Practically no increase in consumption was obtained by continuing the leaching beyond this time.

Leaching at temperatures lower than 50° C. does not give satisfactory decomposition.

When 18 per cent HCL is heated to at least 40° C. before the addition of the feed the heat of reaction is sufficient to raise the temperature of the pulp to 70°C. and this temperature can be maintained without added heat for some time

(Conclusions from Small-Scale Tests, cont'd) -

depending on heat insulation used.

In leaching this feed in 18 per cent HCl at 50-70° C. the acid distribution is approximately as follows:

	<u>Per cent</u>
In forming MgCl <sub>2</sub>	- 86-87
" " chlorides of Fe, Al and Ni	- 11-12
Retained in residue (as chlorides)	- 0.05-0.09
Unused	- 1.4 - 2.0.

This does not take into account the HCl lost by volatilization.

The filtering rate of leach liquor is rather slow but not unpractical.

The chloride retention of the residue is low, averaging 0.2 per cent as 18° Bé HCl or 0.06 per cent of the acid used.

With this practice the MgO extraction is about 70 per cent. This rather low extraction is due to the fact that an excess feed is used to ensure a high utilization of the acid.

#### Purification.

The use of additional waste rock as a precipitant after oxidizing the leach liquor with Cl gas does not appear attractive. A second stage of purification would be necessary.

The other precipitants used gave satisfactory purification of the unoxidized leach liquor.

Calcined waste rock is a very efficient precipitant but would probably be more expensive than prepared magnesium precipitants.

Prepared brucite, basic magnesium carbonate, and MgO are satisfactory precipitants.

Each of these under proper conditions gives a MgCl<sub>2</sub>

(Conclusions from Small-Scale Tests, cont'd) -

of a suitable degree of purity.

The chloride retention is not sufficiently high to cause serious HCl losses.

The hydroxide precipitate is bulky and the filtration rate slow. A large filtering surface is required.

Difficulties are encountered when the precipitants are added to the undiluted leach liquor containing 16-17 per cent  $MgCl_2$ . Purification can be obtained by using  $MgO$  but there is a strong tendency for the formation of oxychlorides. Some stage of dilution less than that used may be practical.

Leaching and Purifying without an Intermediate Filtration.

The waste rock may be leached by the routine method, the pulp diluted and purification obtained by adding brucite and following the practice for purifying the leach liquor.

This practice has the advantage of eliminating one filtration. The time required for removing the total solids was no greater than that required for removing the insoluble residue. The chloride retention was not high.

Basic carbonate did not give complete purification in this procedure.

None of the precipitants gave satisfactory purification when used in an undiluted pulp.

When basic carbonate is used in either the diluted or undiluted pulp the chloride retention is very low. If a second stage of purification were used, this method might have possibilities.

Leaching, diluting and purifying by means of brucite was found the preferable method of obtaining the purified solution in laboratory tests.

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(Conclusions from Small-Scale Tests, cont'd) -

General -

By leaching asbestos waste rock with HCl and purifying the solution with MgO (or its equivalent) a MgCl<sub>2</sub> solution of a high degree of purity can be produced. The purity of the solution is of the following order, based on Mg content:

		<u>Per cent</u>
Total Fe	-	0.002
Ni	-	0.004
Cr	-	0.0004
Si	-	0.008
Al	-	No suitable test available.
Ca	-	Faint trace.

No other impurities found.

These results were obtained by tentative methods and are regarded only as indicative of the degree of purity.

When 500 units of this feed were leached with 1,552 units of 18 per cent HCl about 2,000 units leach liquor was produced. This contained about 320 units MgCl<sub>2</sub>. Due to enrichment during purification the MgCl<sub>2</sub> content was increased to about 365-370 units, this is equivalent to 90-94 units metallic Mg.

When brucite or basic carbonate is used as precipitant, the HCl loss due to chloride retention by the solids is well below 1 per cent of the HCl used for leaching.

The choice among prepared brucite basic magnesium carbonate and calcined waste rock would probably depend on the cost of an equivalent amount of each (based on its precipitating value) and the effect of each on the whole circuit.

The results here detailed formed a basis for large-scale tests, the results of which are described in the following pages, which constitute the second section of Part II.



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Laboratory Investigation

Large-Scale Tests.

Test Procedure:

Approximately 4,077 pounds of asbestos waste rock, which had been received for the large-scale tests, was first ground through 35 mesh and then treated by tabling to remove the free magnetite. The table tailings were dewatered and dried prior to the leaching treatment.

The results of this tabling were as follows:

Product	Weight, per cent	Assays, per cent		Distribution of Fe, per cent
		Fe	MgO	
Feed	100.0	6.61		100.0
Table concentrate	5.2	29.92		23.5
Table tailing	94.8	5.34	36.02	76.5

Although these results were not very good a considerable amount of the harmful magnetite was removed.

The table tailing which was retained for the leaching process gave the following analysis:

	<u>Per cent</u>
Magnesia (MgO)	- 36.02
Lime (CaO)	- 0.55
Silica (SiO <sub>2</sub> )	- 38.82
Alumina (Al <sub>2</sub> O <sub>3</sub> )	- 1.50
Iron (Fe <sub>2</sub> O <sub>3</sub> )	- 4.55
" (FeO)	- 2.20
" (Fe)	- 0.45
Iron (Total Fe)	- 5.34
Chromium oxide (Cr <sub>2</sub> O <sub>3</sub> )	- 0.29
Nickel (Ni)	- 0.19

In the leaching tests a total of 12 batches of rock



(Test Procedure, cont'd) -

were treated. In general, the treatment involved either

(A) leaching the rock with hydrochloric acid solution at elevated temperatures, removing the chloride solution from the waste rock, and precipitating out impurities with magnesia, from which pulp the magnesium chloride solution is removed by a second stage of filtration,

or,

(B) leaching the rock with hydrochloric acid, diluting this leach solution to approximately 10 per cent  $MgCl_2$  content and precipitating out impurities with magnesia; the magnesium chloride solution is removed from this pulp by a single filtration.

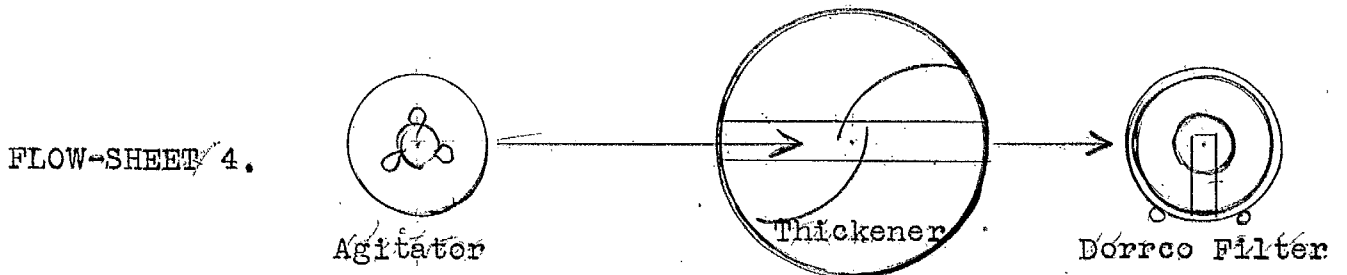
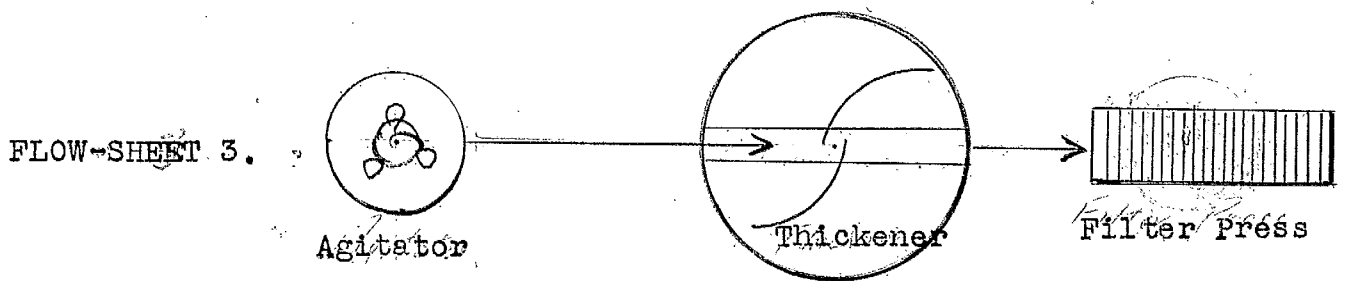
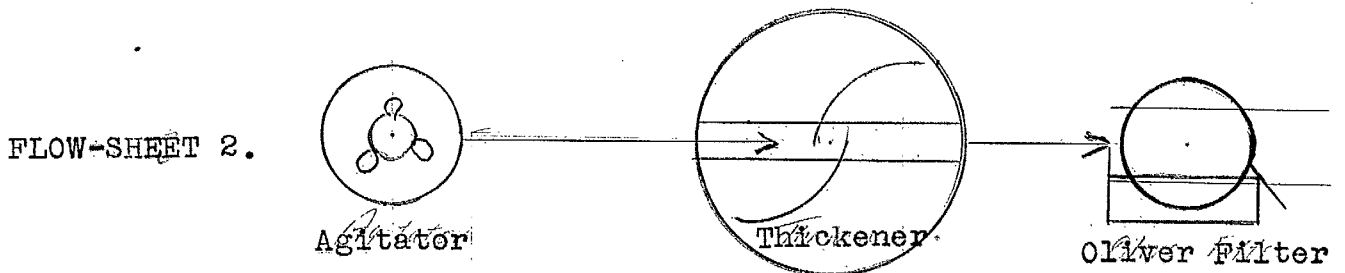
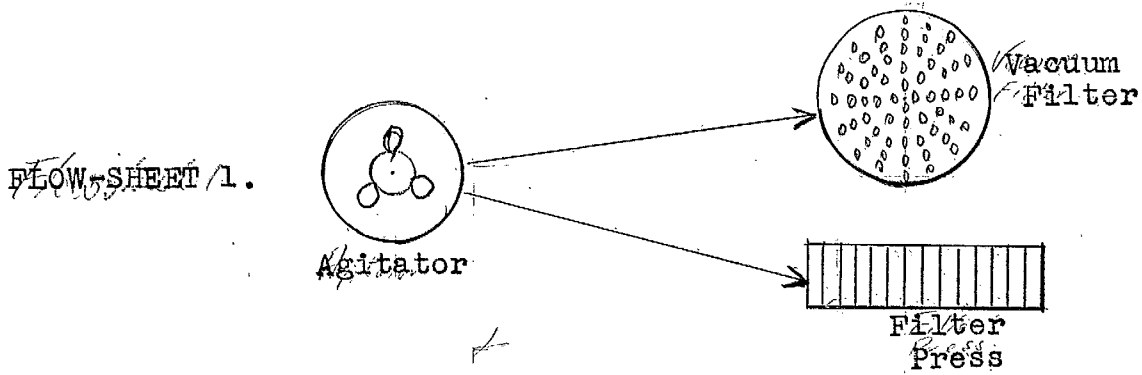
The results obtained using procedure A were unsatisfactory and are not being reported as better results were obtained in the small-scale tests.

In the tests grouped under procedure B, various types of equipment were utilized to try to approximate conditions that would be obtained when large-scale continuous equipment would be used.

The various items of equipment used were as follows: Two 100-gallon earthenware leach jars with wooden agitator paddles; one 50-gallon vacuum filter jar and receiver, one 25-gallon vacuum filter jar and receiver, one 30" Hardinge-type super thickener, one 2" Wilfley pump, one 1' x 14" frame filter press, one 42" x 6" Oliver continuous vacuum filter, one 48" x 12" Dorrco continuous vacuum filter, vacuum pumps, and a small steam generator.

(Continued on next page)

The following sketches will illustrate the flow-sheets employed in the various tests;



DETAILS OF LARGE-SCALE LABORATORY TESTS:

Tests Nos. 1 to 3.

In these tests the rock was leached with 18 per cent HCl solution. The solution containing all the chlorides was filtered from the rock material. The filtrate was treated with calcined brucite to precipitate the hydroxides of iron, chromium, nickel and aluminium; these impurities were filtered out to give a pure  $MgCl_2$  solution.

The results of these tests were unsatisfactory and showed little promise. No figures on the large-scale tests are given. Filtration and washing were difficult and Cl retention high.

Test No. 4.

The rock was leached with 18 per cent HCl solution. At the end of the leach period, water was added to reduce the  $MgCl_2$  content of the solution to approximately 10 per cent  $MgCl_2$ . Calcined brucite (8.5 pounds) was added to this pulp and after the pulp was allowed to settle the supernatant liquid was decanted off and the thickened pulp was filtered, one-half in the vacuum filter and the other in the filterpress.

Tests Nos. 5 and 6 (combined).

A larger amount of rock was leached in two batches, the impurities being precipitated with brucite and the pulp pumped to the thickener. The thickened under-flow was discharged to the Oliver filter. The filtrate and thickener overflow were combined and clarified in a Merrill clarifier with precoated leaves.

(Details of Large-Scale Laboratory Tests, cont'd) -

Tests Nos. 7 and 8.

Standard charges of rock (75 pounds) were leached with 18 per cent HCl and the impurities were precipitated with brucite. The pulp was discharged to a Hardinge-type super-thickener. The thickened underflow was pumped at 40 p.s.i. to the filter~~press~~. The thickener overflow, the thickener filtrate, and the press filtrate were combined. The cake in the press was washed once, the press was then broken, and the cake was repulped with hot water and again pumped into the press. The cake contained chlorides to the extent of 0.07 per cent HCl in Test No. 7 and 0.10 per cent HCl in Test No. 8.

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Test No. 9.

A standard charge of rock was treated as in Tests Nos. 7 and 8. The filter cake was not repulped as in the previous tests but merely given two series of washes. The chloride loss seems to be considerably higher when no repulping stage is involved.

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Tests Nos. 10 and 11.

Standard charges of rock were leached with 18 per cent HCl and the impurities precipitated with brucite. The pulp from the superthickener was discharged to the Dorrco vacuum filter. The cake was given a spray wash before it was discharged. The filter cake was repulped and refiltered twice to give an indicated chloride loss of 0.3 per cent HCl after the first refiltration and 0.18 per cent after the second refiltration.

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(Details of Large-Scale Laboratory Tests, cont'd) -

Test No. 12.

A standard charge of rock was leached with 18 per cent HCl and after dilution the impurities were precipitated using 5.0 pound of C.P. MgO. In other respects this test was similar to Tests Nos. 10 and 11.

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Flow-sheet 1 was used in Test No. 4, where the pulp after precipitation was run half to the vacuum filter and half to the filter press.

Flow-sheet 2 was used in Tests Nos. 5 and 6 where the pulp after precipitation was pumped to the 30" thickener. The underflow was filtered in the Oliver filter.

Flow-sheet 3 was used in Tests Nos. 7, 8, and 9. In these tests the Hardinge-type superthickener was being used, followed by the filter press.

Flow-sheet 4 was used in Tests Nos. 10, 11, and 12. This was in all respects the same as Flow-sheet 3 but the Dorrco vacuum filter was employed in place of the pressure filter.

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The results of these various tests are given in tabulated form, as follows:

(Continued on next page)

(Details of Large-Scale Laboratory Tests, cont'd)

Test No.	Weight of rock, pounds	Weight of 18% HCl solution, pounds	Average temperature, degrees C.	Time of leach		MgCl <sub>2</sub> Solutions,			Filter Cake		
				hrs.	mins.	Filtrate	1st Wash	2nd Wash	Chlorides as HCl, per cent	Per cent moisture	
<u>4</u> (Flow-sheet 1)	75	216	65	3		11.70	4.85 F.P. 6.1 V.F.	-	1.40 F.P. 3.24 V.F.	10.0 F.P. 30.0 V.F.	
<u>5</u> and <u>6</u> , combined (Flow-sheet 2)	285	825	73.5	1	45	12.41	-	-	2.78	35.0	
<u>7</u> (Flow-sheet 3)	75	216	73	2		9.50	1.34	0.23	1st Wash : 0.47 2nd Wash : 0.07	19.0	
<u>8</u>	75	216	75	1	45	10.58	1.47	0.38	0.82 : 0.10	11.0	
<u>9</u>	75	216	65	3		10.90	1.39	0.305	1.03	7.0	
<u>10</u> (Flow-sheet 4)	75	216	67	2	30	9.1	1.8	0.37	0.27 : 0.16	35.0	
<u>11</u>	75	216	75	1	30	11.0	2.0	0.5	0.31 : 0.18	37.0	
<u>12</u>	75	216	69	2		9.45	2.9	0.9	1.2 : 0.66	36.0	

F.P. - Filter Press.

V.F. - Vacuum Filter.

(Details of Large-Scale Laboratory Tests, cont'd) -

Additional data obtained from these large-scale tests were as follows:

Ratio, solution to solids in leach - 3.1:1.

Optimum temperature of leach, 70° to 75° C.

Minimum time of leach - 1 hour 30 min.

Recommended time of leach - 3 hours.

Final acid value of leach - 0.3 per cent HCl, or less.

Ratio of solution to solids in precipitation - 5.5:1.

Weight of precipitant -

Magnesia (Brucite) - 8.5 pounds.  
(MgO C.P.) - 5.0 "

Final pH of solution - 7.0 to 7.3.

Settling rate of pulp after precipitation, 0.75 ft. per hr.

Ratio of solution to solids after settling, 1:1.

Recommended thickener area - 9 sq.ft./ton/24 hrs.

Approximate filtering rates:

Filter press, 150-250 lb./sq.ft./24 hrs.  
Oliver filter, 150-200 " "  
Dorrco filter, 250-900 " "

#### CONCLUSIONS FROM LARGE-SCALE TESTS:

It appears, from the results of these various tests, that it will be possible to extract a magnesium chloride solution of high purity from the asbestos waste rock material which has been submitted for treatment.

The indicated equipment and flow-sheet for the leaching and precipitation plant are quite simple. The initial leaching tanks will, of course, have to be of acid-proof construction and the first precipitation tank will have to resist moderate concentrations of ferric chloride. However, the remainder of the equipment can be standard in all respects. It is obvious

(Conclusions from Large-Scale Tests, cont'd) -

that since standard flow-sheet and equipment may be used the cost of the leaching plant need not be excessive.

There are some details which will have to be worked out in a full-scale plant. The 18 per cent HCl solution has been used, in that this strength of acid gives rapid action on the rock with a minimum loss of hydrochloric acid. Loss of HCl by volatilization over the leaching tanks has not been determined but it seems possible that suitable ventilating-collecting equipment could be installed to minimize this loss.

In the purification stage the number of washes that the filter cake must be given will likewise have to be considered from the standpoint of capital expenditure for filtering equipment compared with the chloride recovery effected. In all the tests, the chloride retention has been very low. Washing alone gives good chloride removal.

The source of the magnesia for the precipitation of the impurities, whether it is produced from magnesium chloride or whether calcined brucite is used, will depend on the relative costs of the materials.

A point which was of interest was the fact that the temperature had considerable bearing on the rate of the leaching action. The temperature at which the most rapid action occurred was 75° C. Higher temperatures are not to be recommended, however, owing to the likelihood of formation of gelatinous silica.

A solution of higher magnesium chloride content would be advantageous, but, in view of the reactions involved, namely high chloride retention in precipitate and formation of oxy-chloride (which are discussed in the section on small-scale experimental work), it would appear that there is a limit which



(Conclusions from Large-Scale Tests, cont'd)-

should not be exceeded. This limit may be higher than the 10 per cent  $MgCl_2$  used in these tests.

The recommended flow-sheet will be found in the first section of the report.

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