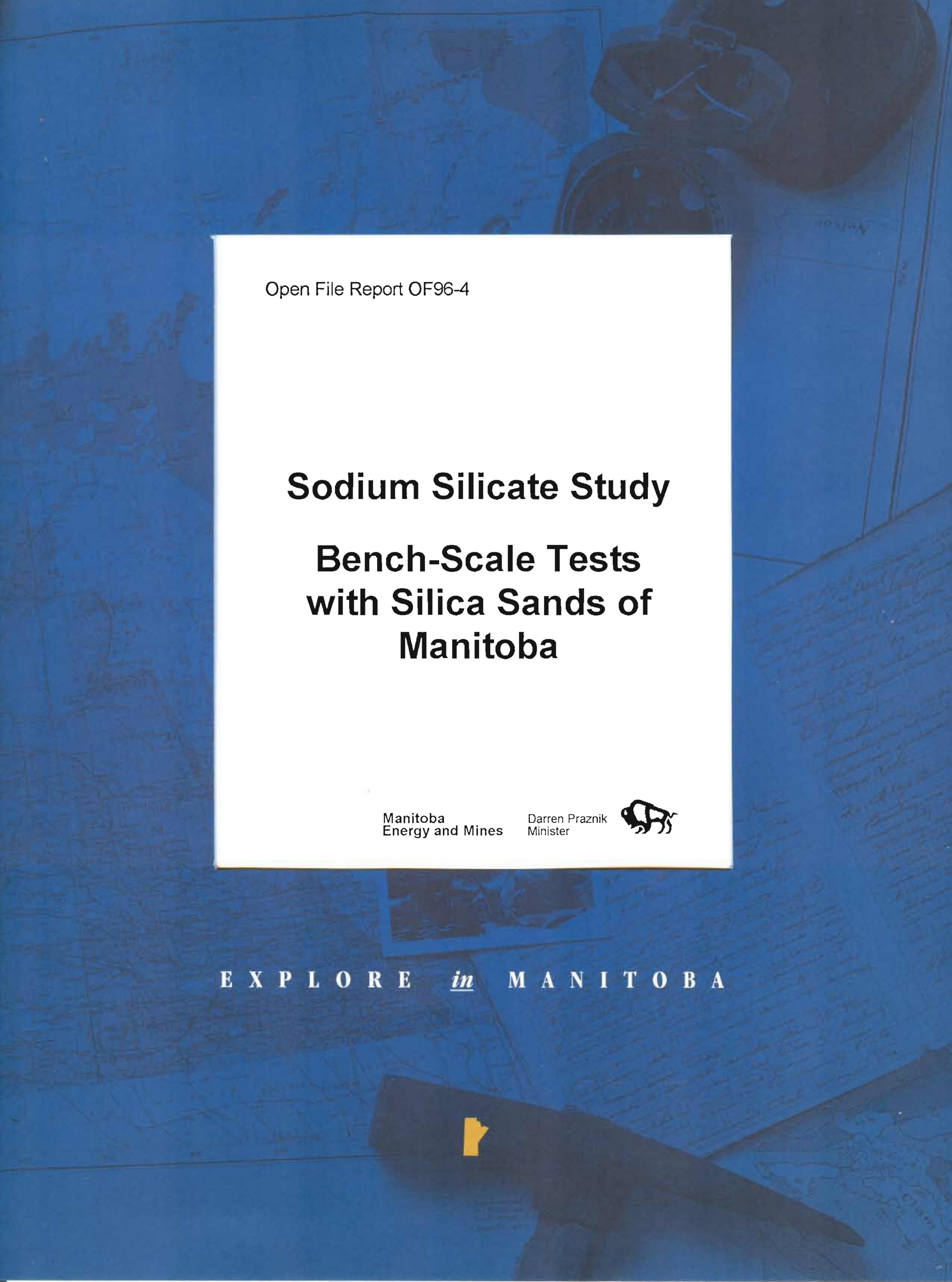

Open File Report OF96-4

Sodium Silicate Study

Bench-Scale Tests with Silica Sands of Manitoba

Manitoba
Energy and Mines

Darren Praznik
Minister

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Manitoba
Energy and Mines
Marketing Branch

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Sodium Silicate Study Bench-Scale Tests with Silica Sands of Manitoba

by Ash Associates
Toronto, Ontario
1996

Energy and Mines

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Minister

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Deputy Minister

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This publication is available in large print, audiotape or braille on request

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EXECUTIVE SUMMARY

Laboratory trials were conducted in the fourth quarter of 1995 to ascertain the suitability of selected silica sand deposits in the province of Manitoba as a raw material resource for the manufacture of sodium silicates.

The test program was developed by ASH ASSOCIATES of Toronto, Ontario and carried out by I.M.D. Laboratories Ltd. and ORTECH Corporation, both located in Ontario.

SAND BENEFICIATION TESTS

The first stage of the program was the beneficiation of two composite silica sand samples, representing the Swan River Formation and the Black Island deposits of the Winnipeg Formation in Manitoba. Standard processing methods of de-sliming, attrition scrubbing,including acid scrubbing, magnetic separation and screening were employed to upgrade the test samples to the sizing and chemical requirements required by sodium silicate producers.

The beneficiation tests demonstrated that the Black Island sand of the Winnipeg Formation is a good high-purity material that can be readily processed to meet current industry specifications and only needed a small reduction in CaO content to achieve a more stringent premium grade for sodium silicate manufacture. Product recovery from this sample was reported as 82.4%.

Upgrading tests on the Swan River Formation sample persistently failed to meet the primary specification limit of 0.2% max. alumina content. The fineness of this sand also makes it unattractive for processing into a minus 30 plus 100 U.S. mesh product, with 85% of the particle size distribution between 70 and 100 mesh, and low product recoveries of the order of only 40%.

MELT FUSION TESTS

Commercial-grade raw materials were procured for the fusion trials. Illinois silica sand was obtained for use as an industry standard for comparative evaluation of performance. Natural sodium carbonate (trona) was procured from Wyoming and mixed together with the beneficiated silica sand materials at a theoretical ratio of 3.22 SiO_2 to 1.00 Na_2O.

Scoping tests were first performed by ORTECH in a platinum crucible to determine the temperature of CO_2 evolution, foaming characteristics and optimal molten flow temperature. Four melt fusion trials were subsequently carried out in larger silicon carbide crucibles, including one run each using the Winnipeg Formation and Swan River Formation sands and two using the Illinois sand standard; each run was held at temperature levels of 900 C. and 1,350°C.

Quenching of the molten fused product produced a well-fractured glass product of approximately minus 4 mesh (4.75 mm). Variability of the SiO_2:Na_2O ratios from a theoretical 3.22 to 3.62 (Swan River Formation test) and 3.75 (Winnipeg Formation sand) is assumed by ORTECH to be due to Na volatility. The oxide impurity levels for solid sodium silicates were reported to be within industry guidelines with the exception of alumina in the product using the Swan River Formation sand.

SILICATE DISSOLUTION TESTS

Liquid sodium silicate (water glass) was produced in a 2-litre pressure autoclave. Solids to water ratios of 2.5:1 were mixed for 5 hours at an average temperature of 170°C. Filtered volumes of 1090 and 1100 millilitres were produced for the Swan River Formation and and Winnipeg Formation trial runs respectively.

The production of clear, bright water glass that fell within prescribed ranges for specific gravity and SiO_2:Na_2O ratios was reported by ORTECH. The selected oxide analyses were also reported to be within industry standards, with the continued exception of alumina in the run using Swan River material. The Swan River run also left an undissolved glass residue following water glass production.

It is concluded that the overall performance of the Winnipeg Formation material in the bench-scale tests was very encouraging and warrants further consideration as a raw material for sodium silicate manufacture. The problems of particle size distribution, impurity levels and low product recoveries in processing the silica sands of the Swan River Formation, however, are significant drawbacks to meeting the requirements of the sodium silicate industry.

SOMMAIRE DE DIRECTION

Des essais en laboratoire ont été effectués durant le dernier trimestre de l'année 1995 pour étudier la possibilité d'utiliser le sable silicieux de certains gisements de la province du Manitoba comme source de matière première dans la manufacture de silicates de sodium.

Le programme de tests a été élaboré par ASH ASSOCIATES de Toronto (Ontario) et effectué par les sociétés I.M.D. Laboratories Ltd. et ORTECH Corporation, toutes deux situées en Ontario.

TESTS D'ENRICHISSEMENT DU SABLE

La première étape du programme a été l'enrichissement de deux échantillons composites de sable silicieux représentant la formation Swan River et les gisements Black Island de la formation de Winnipeg au Manitoba. Des méthodes de traitement courantes telles que le déschlammage, l'attrition par débourbage ainsi que le débourbage acide, la séparation magnétique et le tamisage ont été employées pour enrichir les échantillons afin que leur répartition granulométrique et leur contenu chimique répondent aux exigences des producteurs de silicates de sodium.

Les tests d'enrichissement ont démontré que le sable Black Island de la formation de Winnipeg est une matière de haute pureté qui peut facilement être traitée selon les spécifications industrielles actuelles et qui ne requiert qu'une petite réduction de son contenu de CaO pour atteindre la plus haute qualité nécessaire à la manufacture de silicates de sodium. La récupération de produit de cet échantillon a été évaluée à 82,4 %.

Les tests d'enrichissement effectués avec l'échantillon de la formation Swan River n'ont pas réussi à garder le contenu maximum d'alumine à 0,2 %, limite de la spécification principale. De plus, à cause de la finesse de ce sable, il est peu intéressant de le traiter pour en faire un produit de moins 30 plus 100 mailles US, car 85 % de la répartition granulométrique de ses particules se situe entre 70 et 100 mailles et la récupération de produit, de l'ordre de seulement 40 %, est basse.

TESTS DE FUSION

Des matières premières de calibre commercial ont été obtenues pour les essais de fusion. Du sable silicieux de l'Illinois a été utilisé comme standard industriel à des fins d'évaluation comparative des résultats. Du carbonate de sodium naturel (trona) a été obtenu du Wyoming et ajouté au sable silicieux enrichi dans un rapport théorique de 3,22 SiO_2 à 1,00 Na_2O.

D'abord, des tests d'étendue ont été effectués par ORTECH dans un creuset de platine afin de déterminer la température de l'évolution du CO_2, les caractéristiques moussantes et la température d'écoulement optimale de la matière fondue. Quatre essais de fusion ont subséquemment été effectués dans de plus grands creusets en carbure de silicium, dont un test chacun pour les sables de la formation de Winnipeg et de Swan River, et deux tests pour le sable standard de l'Illinois. Pour chaque test, la température a été maintenue à des niveaux de 900 °C et 1350 °C.

La trempe du procuit fusé a produit un verre bien fracturé d'environ moins 4 mailles (4,75 mm). Le fait que la variabilité du rapport SiO_2 : Na_2O soit passée de la valeur théorique 3,22 à 3,62 (test de la formation Swan River) et à 3,75 (la formation de Winnipeg) dépendrait, selon ORTECH, de la volatilité du Na. La temeur en impuretés oxydées des silicates de sodium solides était conforme, selon les rapports, aux exigences de l'industrie, sauf pour ce qui est de l'alumine contenue dans le produit provenant des sables de la formation Swan River.

TESTS DE DISSOLUTION DU SILICATE

Du silicate de sodium liquide (verre soluble) a été produit dans un autoclave à pression de 2 litres. Dans une proportion de 2,5 contre 1, les solides et l'eau ont été mélangés pendant 5 heures à une température moyenne de 170 °C. Les tests effectués avec les sables de la formation Swan River et de la formation de Winnipeg ont produit, respectivement, des volumes filtrés de 1090 et de 1100 millilitres.

ORTECH a rapporté avoir produit du verre soluble clair et brillant dont la gravité spécifique et les rapports SiO_2 : Na_20 se situaient à l'intérieur des limites prescrites. En outre, des analyses sélectives d'oxydes ont démontré qu'ils étaient conformes aux normes industrielles, à l'exception de l'alumine qui a continué d'entacher le matériel provenant de la formation Swan River. Il a également été noté, après le test effectué avec le matériel Swan River, qu'il restait un résidu de verre non dissous après la production de verre soluble.

On peut donc conclure que la performance générale du matériel de la formation de Winnipeg mis au banc d'essai est encourageante et justifie sa considération comme matière première dans la manufacture de silicates de sodium. Cependant, la répartition granulométrique des particules, les niveaux d'impureté et la faible récupération de produit résultant du traitement des sables silicieux de la formation Swan River constituent des problèmes importants qui empêchent de satisfaire aux exigences de l'industrie des silicates de sodium.

GENERAL INTRODUCTION

Sodium silicates are water-soluble synthetic products that are commonly manufactured by fusing high-purity silica sands and sodium carbonate at high temperatures.

Commercial soluble silicates form three groups of products:

a) anhydrous solids - as glasses or powders formed by fusion processes. The two main types are 3.2 and 2.0 ratio grades (SiO_2:Na_2O ratio);
b) hydrous solids - sodium metasilicates formed by hydration of glasses or evaporation of solutions;
c) liquids - the largest category in terms of sales volume; they are differentiated by the ratio of SiO_2 to Na_2O and by specific gravity.

Sodium silicates are produced in over 30 plants in North America with a combined production capacity exceeding one million tonnes. The largest single use is as an additive is in soaps and detergents, accounting for close to one-third of production. They are also an important source to the chemical industry for the manufacture of silica-based derivatives such as precipitated silica, silica gels and sols, pigments, synthetic zeolites and clays. The manufacture of derivatives accounts for about half of the total annual production of soluble silicates. Other prominent applications include water treatment, ore flotation in mineral beneficiation, paper adhesives and cement binders.

OBJECTIVE

The test work was designed to obtain a preliminary indication of the suitability of high-purity silica sands from the Winnipeg and Swan River Formations of the Province of Manitoba, represented by samples provided by Manitoba Energy and Mines for bench-scale testing, as a raw material in the production of sodium silicates of commercial grade.

The test program is part of a larger study to determine the economic parameters of sodium silicate production in Manitoba that is being conducted under the Canada/Manitoba Partnership Agreement.

WORK PROGRAM

The work program selected to meet the objective within the constraints of the fixed budget consisted of three stages:

1. treatment of raw silica sand samples by standard beneficiation procedures to meet the sizing and chemical specifications of the sodium silicate manufacturing industry.

   Composite samples of silica sand were provided to I.M.D. Laboratories on September 22, 1995 to start the test program as follows:

   - 19.6 kilograms of untreated silica sand from the Winnipeg Formation (Black Island) in Manitoba;
   - 8.3 kilograms of untreated silica sand from the Swan River Formation in Manitoba.

   A primary level of specifications was set by ASH ASSOCIATES for beneficiated silica sand for both particle size limits and chemical requirements for selected oxide values.

   ASH ASSOCIATES further required that reasonable processing efforts be used to investigate whether the samples could provide a premium quality product to meet the following more stringent chemical specifications for the oxides of aluminium, calcium and magnesium.

2. Bench-scale melt fusion tests, using beneficiated silica sand test materials and sodium carbonate (soda ash) to produce a 3.2 ratio grade of sodium silicate.

   Commercially-available trona, natural sodium carbonate of appropiate grade from Wyoming, U.S.A., was procured for the melt tests. Commercially-available treated silica sand from Illinois, U.S.A., of appropiate grade for sodium silicate manufacture, was also procured as a test standard.

3. Autoclave dissolution tests to produce liquid sodium silicate products. Chemical analyses of the sodium silicate products were required for the following oxides: SiO_2 CaO MgO Fe_2O_3 TiO_2 Al_2O_3

   The density, viscosity, silicate content and level of metal impurities for each solution product were also factors to be measured in the program.

   ASH ASSOCIATES contracted the services of I.M.D. Laboratories Ltd. in Barrie, Ontario for the execution of the first stage of the study and the delivery of beneficiated silica sand products. The tests were supervised by Jack Kriens, President of I.M.D. Laboratories.

   ORTECH Corporation of Mississauga, Ontario was contracted for the melt fusion and dissolution tests of the work program, using the upgraded silica sand samples. This portion of the program was conducted by Marc Rishea and Patrick Tackaberry of the Separation Technologies Section of ORTECH Corporation.

PART I

BENEFICIATION OF NATURAL SILICA SANDS OF THE WINNIPEG AND SWAN RIVER FORMATIONS IN MANITOBA

By:

J.Kriens
I.M.D. LABORATORIES LTD.
Barrie, Ontario

Report No: 95020

1.0 SUMMARY

Processing studies were undertaken to investigate the potential of beneficiating two distinct types of natural sands from the Winnipeg Formation (Black Island) and Swan River Formation of Manitoba. The results of these studies are outlined below.

1.1 WINNIPEG FORMATION SAND

The Winnipeg Formation (Black Island) sand can be upgraded to the required purity as specified using a combination of blunging the sand with water and a dispersant followed by removal of slimes and fines. Following this the sand fraction is processed by attrition scrubbing at 75% solids, adding 10 kg/tonne of 96% sulphuric acid to the pulp.

Additional slimes and fines generated during this process were removed by washing and screening, after which the sand slurry was filtered and dried. The dried sand was then processed by dry high intensity magnetic separation. The separated product was screened at 30 and 100 mesh to remove +30 mesh oversize and residual -100 mesh fines.

Product derived from the above processing steps resulted in material in compliance with specified objectives of chemical purity and size distribution, with the exception of the CaO content of the final product which exceeded the specified 0.005% CaO level of the premium quality product.

Product recovery of "specification sand" produced from the Winnipeg Formation sand was calculated to be 82.4%. It is expected that recovery in a commercial processing plant will be in the range of 80-85%.

1.2 SWAN RIVER FORMATION SAND

Material from the Swan River Formation could not be efficiently processed with the above described processes.

The material is very fine; 80-85% of the sand is concentrated within the size range 70 to 100 mesh. Under laboratory conditions it was difficult to achieve the required quality with respect to size distribution. Under typical industrial plant conditions it would be very difficult to process this type of sand.

It was not possible to achieve the 0.2% maximum for Al_2O_3 as required. Because of these process and purity difficulties the Swan River Formation deposit should not be given further consideration as a potential resource, unless sand with a coarser size distribution can be located in this deposit. Product recovery for the Swan River material was only 40% of an "off specification" product.

Final products as produced were forwarded to Ash Associates for the purpose of conducting tests to produce sodium silicate.

Summary Tables S-1 and S-2 give the analytical data on both sample materials at various stages of processing while, Table S-3 gives the size distribution of the final products produced.

Table S-1: Chemical Analysis - Winnipeg Formation (Black Island Sand)

Element	Crude Sand As Received By XRF ** %	Attrition Scrubbed Washed-Deslimed By XRF %	Magnetic Separation Product By XRF %	Acid Scrubbed Product By XRF %	By ICP *** %	By AA **** %
SiO_2	98.13	99.55	99.60	99.70		
Al_2O_3	0.84	0.11	0.11	0.04	0.0404	0.053
CaO	0.07	0.02	0.01	<0.01	0.0119	0.018
MgO	<0.05	<0.05	<0.05	<0.01	0.0025	0.0041
Na_2O	<0.05	<0.05	<0.05	<0.01		0.0027
K_2O	0.05	0.01	0.01	<0.01		
Fe_2O_3	0.14	0.055	0.045	<0.01	0.0113	0.0126
MnO	0.01	0.01	0.01	<0.01		
TiO_2	0.07	0.02	0.01	0.001		
ZrO_2	--	0.013	0.008			
Cr	--	N.D. *	N.D.	<0.01		
L.O.I.	0.59	0.11	0.10	0.30		

The Winnipeg Formation sand meets the first and second level purity, with the exception of the 0.005% CaO required for the highest purity level.

Table S-2: Chemical Analysis - Swan River Formation Sand

Element	Crude Sand As Received BY XRF ** %	Attrition Scrubbed Washed-Deslimed By XRF %	Magnetic Separation Product By XRF %	Acid Scrubbed Product By XRF %	By ICP*** %	By AA**** %
SiO_2	95.14	99.07	99.18	99.70		
Al_2O_3	1.65	0.27	0.29	0.29	0.27	0.32
CaO	0.16	0.01	0.01	<0.01	0.0115	0.014
MgO	0.14	<0.05	<0.05	<0.01	0.0058	0.006
Na_2O	0.05	<0.05	<0.05	<0.01		
K_2O	0.37	0.15	0.16	0.11		
Fe_2O_3	0.74	0.10	0.05	0.02	0.0243	0.027
MnO	0.02	0.02	0.02	<0.01		
TiO_2	0.30	0.15	0.04	0.023		
ZrO_2	--	0.066	0.035			
Cr	--	N.D. *	N.D.	<0.01		
L.O.I.	1.49	0.16	0.14	0.25		

The Swan River sand does not meet the required first or second level purity requirement of 0.2 and 0.1% alumina respectively.

N.D.	Not Detected
XRF	X-ray Fluorescence Spectrometry
ICP	Induced-Plasma Atomic Emission Spectrometry
AA	Atomic Absorption Spectrometry

Table S-3: Size Distribution of Final Sand Products

	Winnipeg Formation Black Island Sand		Swan River Formation		
Mesh Size	% Individual	% Cumulative	% Individual	% Cumulative	
	+ trace	30	0.08	0.08	trace
- 30 + 40	7.88	7.96	0.16	0.16	
- 40 + 50	22.66	30.62	2.93	3.09	
- 50 + 70	34.72	65.34	7.41	10.50	
- 70 +100	33.76	99.10	85.44	95.94	
-100 +140	0.88	99.98	3.68	99.62	
- 140	0.02	0.02	0.38	0.38	
	100%	**100%**	**100%**	**100%**	

The stated specification of maximum 0.12% on 30 mesh is readily achieved. The specification of maximum 2% passing 100 mesh is much more difficult to obtain and could not be realized with the Swan River sand.

2.0 INTRODUCTION

Ash Associates provided I.M.D. with a detailed description of product quality requirements for silica sands suitable for the manufacture of sodium silicate. The quality objectives are listed below.

These requirements were to be achieved if possible by commonly accepted mineral processing techniques and only if this failed to produce product of acceptable quality, other less commonly processing techniques were to be investigated.

SIZE ANALYSIS OF PRODUCTS

Minus 30 mesh plus 100 mesh with a maximum of 0.12% on 30 mesh and 2% maximum passing 100 mesh.

CHEMICAL PURITY - FIRST LEVEL

SiO_2	99.4%
Fe_2O_3	0.03% maximum
Al_2O_3	0.2% maximum
TiO_2	0.05% maximum
CaO	0.05% maximum
MgO	0.05% maximum

CHEMICAL PURITY - PREMIUM QUALITY PRODUCT

Al_2O_3	0.10% maximum
CaO	0.005% maximum
MgO	0.01% maximum

PRODUCT VOLUME TO BE PRODUCED

Approximately 4 kg of the highest quality of product produced by "standard" industrial methodology of each of the two submitted samples.

SAMPLE IDENTIFICATION

One sample was identified as being from the Winnipeg Formation (Black Island, Manitoba). The other sample was identified as being from the Swan River Formation of Manitoba.

The samples were submitted as damp unprocessed sand. In the case of the Winnipeg Formation, several small sub-samples consisting of agglomerated sand nodules were also submitted.

This report describes in detail the processes that were employed to beneficiate the submitted samples to the chemical purity and sizing as required by the product specification.

3.0 PROCESSING CONSIDERATIONS

In the processing of silica whether in rock form, natural sand or friable sandstones, the processing methods employed are usually a combination of size reduction, attrition scrubbing at high solids levels, desliming, washing, filtering and drying, followed by magnetic separation and/or froth flotation.

With natural sands such as the Winnipeg and Swan River materials, size reduction by virtue of crushing etc. is not necessary as most of the material is already reduced to its natural grain size by geological processes. Typically, these type of sands are associated with other minerals such as kaolin clay or carbonates that occur as cementing material and as a coating on the grains. Other associated minerals occur either as free distinctive minerals or as a coating on the sand grains. Iron hydroxide minerals such as goethite or limonite are commonly present.

Microscopic examination showed that the Winnipeg formation sand has a well rounded particle shape, whereas the Swan River sand has the typical high degree of angularity and characteristical conchoidal fracturing. The Winnipeg Formation sand contained mostly kaolinitic fines, occurring as a coating and as a cementing material between grains. The Swan River material is considerably finer and closely sized. Here contaminants consist of a grey coloured clay, muscovite mica and other grey black opaque minerals. It also contains organics which appear to be from leaves or small twigs.

Based on these observations it was clear that both samples required attrition scrubbing to remove kaolin, other slimes as well as unwanted silica fines. The attrition process would also break up soft cemented concretions contained in the samples.

3.1 ANALYSIS OF CRUDE UNPROCESSED SANDS

Each of the submitted samples was reduced in size with a sample splitter and a 1000 gram sample obtained for determination of moisture content, size distribution of the raw sand and chemical composition.

The "as received" weights of the samples was as follows:

Winnipeg Black Island sand	43.1 lb./19.5 kg
Swan River Formation sand	18.2 lb./ 8.3 kg

The moisture content was determined by drying 1000 gram at 110°C for 16 hours. The following results were obtained:

Winnipeg Black Island sand	1.63%
Swan River Formation sand	5.68%

Part of each sample was used for chemical analysis. The analytical method employed was X-ray fluorescence.

Results of these analyses are given in Table 1.

3.1.1

Table 1
Chemical Analyses Crude Unprocessed Sand

	Winnipeg Formation Sand %	Swan River Formation Sand %
SiO_2	98.13	95.14
Al_2O_3	0.84	1.65
CaO	0.07	0.16
MgO	<0.005	0.14
Na_2O	<0.005	<0.05
K_2O	0.05	0.37
Fe_2O_3	0.14	0.74
MnO	0.01	0.02
TiO_2	0.07	0.30
L.O.I.	0.59	1.49

3.1.2 DISCUSSION OF ANALYTICAL RESULTS - CRUDE SAND

The analyses confirm the presence of aluminous and calcitic contaminants in the Winnipeg Formation sand. The Swan River sand, beside clay, indicates the presence of potassium feldspar and/or muscovite mica and a titanium mineral.

3.1.3 SIZE DISTRIBUTION OF CRUDE UNPROCESSED SANDS

Each of the dried unprocessed sands was analyzed for its "as received" size distribution. No effort was made to brake up any of the concretions or agglomerates. Individual size fractions were examined microscopically for presence of agglomerated particles. Results are given in Table 2.

Table 2
Size Distribution of "As Received" Sands

Winnipeg Formation (Black Island)

		% Individual	% Cumulative	Comments
+ 4	Mesh	5.17	5.17	100% agglomerated grains
- 4 + 8	"	2.20	7.37	100% "
- 8 + 12	"	1.41	8.78	100% "
- 12 + 20	"	2.26	11.04	100% "
- 20 + 30	"	2.85	13.89	<10% "
- 30 + 40	"	8.86	22.75	NO agglomerates
- 40 + 50	"	17.23	39.98	NO "
- 50 + 70	"	25.84	65.82	NO "
- 70 +100	"	27.16	92.98	NO "
-100 +140	"	5.57	98.55	NO "
- 140	"	1.45	1.45	NO "
		100%	**100%**	

Swan River Formation Sand

		% Individual	% Cumulative	Comments
+ 20	Mesh	0.99	0.99	100% agglomerated grains
- 20 + 30	"	2.28	3.27	100% "
- 30 + 40	"	3.56	6.83	90% "
- 40 + 50	"	5.69	12.52	50% "
- 50 + 70	"	11.97	24.49	40% "
- 70 +100	"	45.74	70.23	10% "
-100 +140	"	18.87	89.10	< 5% "
- 140	"	10.90	10.90	fine sand
		100%	**100%**	

3.1.4 COMMENTS ON SIZE DISTRIBUTIONS - CRUDE SAND

The particle size distributions given in Table 2 only serve as an indication. The presence of concretions and agglomerates mask the actual size distribution of these sands. In the Winnipeg Formation sands these agglomerates persist down to the 30 mesh size, while in the Swan River sand agglomeration was evident throughout the whole tested size range.

Based on these analyses it became clear that these agglomerated particles needed to be broken up by either aggressive attrition scrubbing or if this was not successful, by some manner of grinding and screening. Physical examination indicated that the agglomerates were friable and were likely to respond to the attrition process. This course of action was taken as the next processing step.

4.0 ATTRITION SCRUBBING - PRELIMINARY TESTS

Preliminary attrition scrubbing tests were conducted on both crude sand samples. These tests were conducted using a Wemco 2 liter attrition cell. 1400 grams of sand were mixed with 350 ml. of water to produce an 80% solids slurry. The attrition cell was operated at 1200 RPM.

It became evident with both of the sands that significant amounts of fine slimes were generated very quickly, which resulted in the slurry becoming viscous and lubricated by excessive slimes. Each of the treated materials was washed and deslimed over a 100 mesh screen to remove slimes and unwanted fines. Washed sands were filtered and dried.

The dried weight of the scrubbed, washed and deslimed sand was recorded and gave the following results as to recovery of sand.

Winnipeg Formation - Black Island	1281.3 gram	=	91.52%
Swan River Formation sand	969.9 gram	=	76.16%

The fines and slimes losses were very high for the Swan River sand. This was expected based on the size distribution of the crude sand which consisted of mostly agglomerated particles.

The generation of slimes and fines were such that it was decided to pre-treat the raw sands by a preliminary washing and desliming step. This was accomplished by agitating 5 kg. samples in a conditioner at approximately 30% solids for 10 minutes. Sodium hexameta-phosphate at the rate of 2 lb/tonne was added to aid in dispersing slimes. This technique is commonly referred to as blunging.

The slurry was then screened over an 18" Sweco vibratory screen equipped with a 100 mesh screen deck. Fines and slimes were discarded with the exception of slimes from the Winnipeg Formation which were collected and dried in order to determine the chemical composition.

The oversize was partially dewatered to obtain a high solids sand which was then processed by attrition scrubbing for 3 minutes at 75% solids in the Wemco attrition cell. This was followed by a second washing and desliming.

Washed sands were filtered and dried and their weight recorded. Recovery of sand was as follows:

4.1 RECOVERY OF PROCESSED SAND

	Initial Weight	Processed Weight	Sand Recovery
Winnipeg Formation	5000 Gram	4576 Grams	91.52%
Swan River Formation	5722 Gram	4534 Grams	78.50%

4.2 ANALYSIS OF ATTRITION SCRUBBED SAND

Products from "single stage" attrition scrubbing and products produced by first blunging the sand, removing the bulk of slimes and fines and then attrition scrubbed, were analyzed for their chemical composition. Size analyses were done on products from the two stage process.

Size distributions are given in Table 3 and chemical analyses on Table 4. In addition to the typical "whole rock" analyses these samples were analyzed for zircon and chrome. Zircon and chromite are refractory minerals that may cause problems in the manufacture of sodium silicate or glass.

4.2.1 SIZE DISTRIBUTION OF SANDS PRODUCED BY TWO-STAGE ATTRITION SCRUBBING PROCESS

Table 3

Mesh Size	Winnipeg Formation		Swan River Formation	
	% Individual	% Cumulative	% Individual	% Cumulative
+ 30 M.	2.9	2.9	0.11	0.11
- 30 + 40 M.	7.78	10.68	0.72	0.83
- 40 + 50 M.	15.71	26.39	1.10	1.93
- 50 + 70 M.	26.84	53.23	4.74	6.67
- 70 + 100 M.	37.72	90.95	54.78	61.45
-100 + 140 M.	8.26	98.21	26.27	87.72
- 140 M.	0.79	100.00	12.28	100.00
	100%	**100%**	**100%**	**100%**

4.2.2 COMMENTS ON SIZE DISTRIBUTION OF PROCESSED SANDS

Despite the extensive washing and desliming there is still approximately 9% of fines present in the Winnipeg Formation sand. By comparison the Swan River sand contains a large quantity of -100 mesh fines. This can be attributed to the fact that most of the sand is concentrated in the range of 70 to 140 mesh. With this level of "near sized" material screening becomes a significant operating problem. It would be near impossible to economically produce a product of the required specification.

Screening is considered impractical at this mesh size and air classification could not achieve an acceptable product without also removing a significant amount of the material coarser than 100 mesh. This factor is considered to be decisive in disqualifying the Swan River sand as a potential raw material source, unless other samples taken from this deposit show a significant improvement in size distribution.

4.3 CHEMICAL ANALYSIS OF PRODUCTS PRODUCED BY SINGLE AND TWO STAGE ATTRITION SCRUBBING

Table 4

Element	Winnipeg Formation Sand		Swan River Sand	
	Single Stage %	Two Stage %	Single Stage %	Two Stage %
SiO_2	99.34	99.55	98.70	99.07
Al_2O_3	0.12	0.11	0.31	0.27
CaO	0.03	0.02	0.02	0.01
MgO	<0.05	<0.05	<0.05	<0.05
Na_2O	<0.05	<0.05	<0.05	<0.05
K_2O	0.01	0.01	0.18	0.15
Fe_2O_3	0.06	0.055	0.14	0.10
MnO	0.01	0.01	0.02	0.02
TiO_2	0.02	0.02	0.33	0.15
ZrO_2		0.013		0.066
Cr		N.D.		N.D.
L.O.I.	0.11	0.11	0.19	0.16

4.3.1 COMMENTS ON CHEMICAL ANALYSIS

The effect of two-stage attrition scrubbing is relatively minimal for the Winnipeg Formation sand but is more pronounced for the Swan River sand. Al_2O_3 is reduced as well as Fe_2O_3 and TiO_2. The reduction in Fe_2O_3 and TiO_2 may be due to improved "overall" fines removal.

The Winnipeg formation sand meets the frist level of product purity required with the exception of Fe_2O_3. The Swan River product does not meet Al_2O_3 and TiO_2 specifications and also contains a significant amount of zircon. The non-compliance with Fe_2O_3 specifications in both cases and also the high TiO_2 level in the Swan River sand indicates the need for magnetic separation or flotation. Magnetic separation, if effective, would be preferable over the higher cost flotation process. Magnetic separation therefore was selected as the next step in the beneficiation process.

No further effort was made to remove any additional fines, primarily because they may be a co-product with the main -30 +100 mesh product. Magnetic separation was therefore performed on the product produced by the "two stage" attrition scrub process.

4.3.2 CHEMISTRY OF SLIMES FROM THE WINNIPEG FORMATION SAND

Slimes obtained from washing the Winnipeg sand following attrition scrubbing, were collected, filtered and analyzed for chemical composition. Results were as follows:

Winnipeg Sand Slimes

	%
SiO_2	68.46
Al_2O_3	18.68
CaO	0.22
MgO	0.45
Na_2O	0.05
K_2O	1.10
Fe_2O_3	1.76
MnO	0.01
TiO_2	0.90
L.O.I.	7.98

4.3.2 COMMENTS

These results indicate the slimes consist of kaolin and fine silica. It is expected that most of the Fe_2O_3 and TiO_2 are associated with the kaolin. The high level of K_2O suggests either a potassium feldspar or the presence of sericitic mica. This can be determined via X-ray diffraction. The analyses suggest that approximately 50% of these slimes are kaolin. Because the volume of slimes are limited it is unlikely that they can be recovered economically. They do represent a problem as far as disposal is concerned as it would be necessary to provide for appropriate settling ponds. Flocculants or alum and sulphuric acid would be required to flocculate the slimes and accelerate settling.

5.0 MAGNETIC SEPARATION

Magnetic separation of the samples was done using an Eriez induced roll dry high intensity magnetic separator.

Each of the two samples were given two passes over the separator at 6000 and 1100 Gauss respectively. Magnetics were collected and weighed and percentages of magnetics and nonmagnetics calculated. Non magnetics were analyzed for chemical composition. Details of the magnetic separations are given in Tables 5 and 6.

5.1 MAGNETIC SEPARATION

Table 5

	Winnipeg Formation		Swan River Formation	
	wt/grams	%	wt/grams	%
Feed	4,476	100	4,406	100
1st. Pass Magnetics	18.3	.41	90.5	2.05
2nd. Pass Magnetics	22.6	.50	48.4	1.09
Total Magnetics	40.9	.91	138.9	3.14
Non Magnetics	4435	99.1	4267	96.84

5.1.1 COMMENTS ON MAGNETIC SEPARATION

Only a very minor amount of magnetics was obtained from the separation of the Winnipeg formation sand. Magnetics contained little visually dark minerals. The level of magnetics from the Swan River sand was higher.The magnetics consisted of sand with opaque inclusions, or as attachments of dark minerals on sand grains and free opaque minerals. Non-magnetics from the Winnipeg sand are very clean, but the "non-magnetics" from the Swan River sand still contain dark non-magnetic particles. Some of these appear to be organic in nature.

5.2 CHEMICAL ANALYSIS OF MAGNETICALLY SEPARATED PRODUCTS

Table 6

	Winnipeg Formation	Swan River Formation
SiO_2	99.60	99.18
Al_2O_3	0.11	0.29
CaO	0 01	0.01
MgO	<0.05	<0.05
Na_2O	<0.05	<0.05
K_2O	0.01	0.16
Fe_2O_3	0.045	0.05
MnO	0.01	0.02
TiO_2	0.01	0.04
ZrO^2	0.008	0.035
Cr	N.D.	N.D.
L.O.I.	0.10	0.14

5.2.1 COMMENTS ON ANALYSIS

Magnetic separation of the Winnipeg Formation sand reduced the Fe_2O_3, TiO_2 and ZrO_2 content. Despite this beneficiation, the Fe_2O_3 level at 0.045 is still in excess of the 0.03% required for the first level of purity. All other elements comply with these requirements.

The Swan River sand benefitted from magnetic separation, particularly Fe_2O_3, TiO_2 and ZrO_2. Despite this improvement, the product still did not achieve the first level of purity.

Based on these results, products were again examined under the binocular microscope. This indicated that, in the case of the Winnipeg Formation, some of the grains show a distinctive yellow-brown staining. This staining is most common in surface pits and cracks in the sand grains. The Swan River sand did not clearly show an apparent reason for the high Al_2O_3. The Al_2O_3 is most likely caused by either potassium feldspar and/or muscovite mica. The grains look otherwise clean with the exception of some dark grey opaque grains.

Previous experience with this type of sand products indicated that product quality can often be improved by conducting the attrition scrubbing process in the presence of sulphuric acid. Additions of 5-15 kg. of sulphuric acid per tonne often resulted in marked improvement in Fe_2O_3 and Al_2O_3 content. To this end a preliminary test was conducted with each of the two materials that had been processed by two staged attrition scrubbing and magnetic separation.

Obviously in an "actual" process sequence attrition scrubbing with addition of acid would follow first stage blunging, washing and fines removal. This would be followed by washing, desliming, filtering, drying and magnetic separation.

Therefore, these additional attrition scrubbing tests were "out of sequence". Unfortunately, all of the Swan River material had been processed so it was not possible to repeat the process.

6.0 ATTRITION SCRUBBING UNDER ACIDIC CONDITIONS

To determine the effectiveness of acid addition to the attrition scrubbing process 1400 grams of magnetic separation product from each sample were attrition scrubbed for 3 minutes at 75% solids. 10 Kg. per tonne of 96% sulphuric acid was added to the process water.

Resulting products were deslimed, washed and dried. Products were analyzed by X-ray fluorescence and by atomic absorption or I.C.P. analysis for some trace elements by two separate laboratories. Results of these analyses are given in Table 7.

Table 7

Chemical Analysis of Acid Scrubbed Sand

Winnipeg Formation

	By XRF %	By I.C.P. %	By A.A. %
SiO_2	99.70	---	---
Al_2O_3	0.04	0.0404	0.053
CaO	<0.01	0.0119	0.018
MgO	<0.01	0.0025	0.0041
Na_2O	<0.01	---	0.0027
K_2O	<0.01	---	---
Fe_2O_3	0.01	0.0113	0.0126
MnO	<0.01	---	---
TiO_2	0.001	---	—
P_2O_5	<0.01	—	—
Cr_2O_3	<0.01	---	---
L.O.I.	0.30	---	---

Swan River Formation

	By XRF %	By I.C.P. %	By A.A. %
SiO_2	99.70	—	---
Al_2O_3	0.29	0.27	0.32
CaO	<0.01	0.0115	0.014
MgO	<0.01	0.0058	0.006
Na_2O	<0.01	---	---
K_2O	0.11	---	---
Fe_2O_3	0.01	0.0243	0.027
MnO	<0.01	---	---
TiO_2	0.023	---	---
P_2O_5	<0.01	---	---
Cr_2O_3	<0.01	---	---
L.O.I.	0.25	---	---

6.1 COMMENTS ON ANALYSIS

At the level of purity achieved the X-ray fluorescence technique is no longer sufficiently accurate and precise. Many of the elements in the samples are approaching the limit of detection for this technique. Both atomic absorbtion and I.C.P. techniques are more suitable for the determination of trace elements.

Results clearly indicate that attrition scrubbing at 75% solids in the presence of 10 kg/tonne of sulphuric acid is effective in improving product purity. This can be attributed to both chemical reaction between acid and soluble components and more effective attritioning because there is very little slimes development.

Based on these results there is a clear indication that the Winnipeg Formation Black Island sand can be beneficiated to the highest level of purity desired with the exception of CaO. The Swan River Formation sand however cannot be sufficiently purified to meet the first level of purity. This is due to the persistently high level of Al_2O_3.

As a follow-up to the preliminary test, all remaining magnetic separation product was attrition scrubbed with 10 kg/tonne of sulphuric acid, washed, filtered and dried.

7.0 FINAL SCREENING

To meet the specifications for particle size distribution each of the products was first screened at 30 mesh, followed by screening at 100 mesh. Screened products were analyzed for their particle size distribution. The following percentages of +30 mesh and -100 mesh were removed.

	Wt % +30 M.	Wt % -100 M.
Winnipeg Formation sand	4.1%	1.16%
Swan River Formation sand	0.27%	12.4

7.1 SIZE DISTRIBUTION OF FINAL SCREENED PRODUCT

Table 8

	Winnipeg Formation Sand		Swan RIver Formation Sand	
	% Individual	% Cumulative	% Individual	% Cumulative
+ 30 Mesh	0.08	0.08	trace	trace
- 30 + 40 "	7.88	7.96	0.16	0.16
- 40 + 50 "	22.66	30.62	2.93	3.0
- 50 + 70 "	34.72	65.34	7.41	10.50
- 70 +100 "	33.76	99.10	85.44	95.94
-100 +140 "	0.88	99.98	3.68	99.62
- 140 "	0.02	100.00	0.38	100.00
	100%	**100%**	**100%**	**100%**

7.1.1 COMMENTS ON FINAL SCREENING

After all of the washing and desliming done on the Swan river sand the product still contained a significant amount of material finer than 100 mesh. Screening removed an additional 12.4% of -100 mesh fines. Despite this the "final" screened product still contained 4.06% of -100 mesh. This can be readily explained.

As is shown by the final screen analysis of the Swan River product 85.44 of the material is between 70 and 100 mesh. This high amount of material right at the screen size makes effective screening virtually impossible, with either laboratory test screens or in a production environment. The sand has an extremely tight size distribution. It is not considered possible to achieve the objectives for size distribution in an operating plant. It may not even be possible or practical with air classification.

The Winnipeg formation sand has a typical "normal" size distribution which can be readily screened or air classified to the desired specifications.

8.0 CONCLUSIONS AND RECOMMENDATION

From the work conducted on the two submitted samples the following conclusions can be drawn:

- The Winnipeg Formation Black Island sand can be readily processed to the desired first level of purity. It also complies with the specifications for the higher purity level with the exception of CaO which is slightly above the desired level.
- The level of purity as demonstrated by the processed sample of Winnipeg sand can be achieved by first blunging the raw sand in water and a suitable dispersant. A log washer or large agitating tank would be required. Slurry from the blunging operation can then be processed in a rake or screw classifier to separate the bulk of the fines from the sand.
- Sand product from the classifier is then attrition-scrubbed in a bank of attrition cells to remove the remaining coatings and fines. It may be possible to incorporate the sulphuric acid at this time or it could be again attrition-scrubbed after fines removal in a second stage attritioning to which the acid is added.
- The final slurry is then diluted with fresh water and dewatered via dewatering cyclones. Cyclone underflow, i.e. the sand can then be filtered followed by drying. The dried sand can then be screened to remove any residual oversize after which it is processed by magnetic separation to remove any magnetic or paramagnetic minerals. Product yield is in the 80-85% range.
- Product from magnetic separation can then be conveyed to storage silos. If the washing and desliming process operate effectively there should be no need for further fines removal.
- The Swan River Formation sand is a very difficult material to process, because of its inherent fine size, containing large quantities of -100 mesh material with the bulk of the remaining sand concentrated between 70 and 100 mesh.
- It was difficult to achieve the size distribution objectives under laboratory conditions. It is considered near impossible to efficiently process this type of sand in a commercial operating plant. Product yield was extremely low with only 2.3 kg. of material being recovered from a total of 5.77 kg. of feed material. This is equivalent to a 40% product recovery.
- In addition to this it was also not possible with the processes investigated to achieve the required purity level for Al_2O_3.
- It is the opinion of I.M.D. Laboratories that material of this type is not a suitable candidate for a commercial operation.
- It is recommended that the Winnipeg Formation Black Island deposit be considered as the mineral resource for producing high quality silica sands for such industrial uses as sodium silicate and glass manufacture, filter sand and foundry sand. The natural rounded grain shape of the Winnipeg formation sand is excellent for foundry usage.
- Further work using additional sample material from different parts of the deposit is considered warranted. This work should focus on optimizing the process and process sequence.
- It is recommended that the Swan River Formation deposit not be considered as a potential feed source unless material of a coarser size distribution can be found in the deposit.

PART II

BENCH-SCALE TESTS FOR THE PRODUCTION OF SODIUM SILICATES

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Report No: 95-T13-B004855

1. INTRODUCTION

Ash Associates contracted ORTECH on October 26, 1995 to conduct 12 weeks of testwork on silica sand from two distinct sources, the Winnipeg and the Swan River formations. The testwork included analysis of the raw material oxides, the sand screen structure, the fusion of sand and soda ash to create solid glass, and the solubilization of that glass to a water glass form. ORTECH has completed a four phase bench scale testwork program to evaluate these silica sand samples as well as the industry standard, Illinois sand, in the production of industrially acceptable solid and liquid glass.

2. MATERIALS AND METHODS

Raw materials used in the production of sodium silicate glass are as follows:

	ORTECH Sample #
Illinois silica sand: UNIMIN corp. (C-109)	95-T13-A0060
Sodium Carbonate (soda ash): FMC (Wyoming)	95-T13-A0061
Winnipeg formation silica sand: client	95-T13-A0070
Swan River formation silica sand: client	95-T13-A0071

The Illinois sand and the soda ash were obtained from the stated manufacturers following a request for common industrial use material. Material characterization began with riffling the as-received silica sand into sample sizes suitable for analysis (~10g) and screen structure (~125g). Sieve screen structure was measured using 14, 20, 28, 35, 48, 65, and 100 mesh Tyler screens on a Rotap agitating machine for 20 minutes.

Silica sand (1005g) and soda ash (535g) were mixed together at a theoretical ratio of 3.22 SiO_2:Na_2O assuming 99.5% purity of both and that the soda ash fully dissociates the CO_2 to Na_2O. Fusion and melting of the mixed material was done in a silicon carbide crucible using a top loading furnace, glow bar heated to a maximum 1450°C. The silicon carbide crucible was changed after the first 2 Illinois melts then after each of the Winnipeg and Swan River melts. The molten glass was quenched in tap water then dried, weighed (ORTECH scale MII# 08764) and ground to minus 6 mesh using an agate mortar and pestle and a Tyler 6 mesh screen.

The production of a sodium silicate solution (water glass) was accomplished with a titanium 2L pressure autoclave using a Parr 4841 controller and J type thermocouple. The mixture was stirred using double 6 blade 45° impellers, 1-4 inches from the bottom. Solid to liquid (MPQ cation/anion free water) of 3:1 and 2.5:1 were mixed for 5 hours at an average temperature of 170°C yielding ~100 psi steam. The resulting water glass was filtered through a 0.45 Millipore apparatus and then measured for total volume and specific gravity.

Analytical testwork on solutions was done using inductively coupled plasma (ICP) for required elements. Mathematical conversion to the oxide was then made. Solids were prepared using aqua regia dissolution followed by filtration (#40 Whatman), ashing the filter, fusion with lithium metaborate and potassium iodide, then diluted in 10% nitric acid for ICP analysis. Mathematical conversion to the oxide followed.

3. RESULTS AND DISCUSSION

Phase 1 - Material Characterization

Table 1 details the screen structure of the as-delivered silica sand raw material. The Illinois material and the Winnipeg material both fell within the client prescribed limits of maximum 5% plus 20 mesh, and maximum 15% passing 100 mesh. The Swan River material passed the 20 mesh grade, however, there was significantly more (28%) of the material passing 100 mesh. Considering that fines may potentially contain the majority of the impurities of silica sand, the presence of an increased amount of fines in the Swan River material could account for the higher Al, Ba, and Zn impurities of the water glass solution (Table 4). Oxide analysis of all the raw materials used indicate that all the required oxides, SiO_2, Fe_2O_3, Al_2O_3, TiO_2, CaO and MgO are under the client prescribed limits (Table 4).

Table 1
Screen analysis of raw material silica sand

	Illinois		Winnipeg		Swan River	
mesh size	weight %	weight % passing	weight %	weight % passing	weight %	weight % passing
+ 4	0	100	0	100	0	100
-14 + 20	0	100	0	100	0	100
-20 + 28	0.8	99.2	0.1	99.9	0	100
-28 + 35	23.5	75.7	6.5	93.4	1	99
-35 + 48	47.8	27.9	17.9	75.5	6	93
-48 + 65	22.7	5.2	33.1	42.4	11.9	81.1
-65 +100	5.2	2	32.8	9.6	50.1	31
- 100	2		9.3		28.7	

Table 2
Selected oxide values of experimental raw materials, fused glass products, water glass solutions and 3.3 SiO_2:Na_2O industrial solid glass standards

	oxide weight %							
	CaO	MgO	Fe_2O_3	TiO_2	Al_2O_3	SiO_2	Na_2O	SiO_2:Na_2O
Na_2CO_3	0.00900	<0.01	0.0027	<0.001	<0.01	0.01	>97 (Na_2CO_3)	
ILLINOIS 1								
silica sand	0.006	<0.008	0.010	<0.0017	0.0208	>99.7	<0.0027	
fused glass	0.035	0.094	0.0036	0.016	0.31	74.5	21.3	3.50
ILLINOIS 2								
fused glass	0.080	0.101	0.0051	0.013	0.27	68.5	21.0	3.26
water glass 3:1	0.0005	0.0009	0.006	0.004	0.044	20.9	5.62	3.72
ILLINOIS 2								
water glass 2.5:1	0.0004	0.0009	0.006	0.004	0.047	23.4	6.45	3.63
WINNIPEG								
silica sand	0.0045	<0.008	0.0063	<0.001	0.0051	>99.8	0.0058	
fused glass	0.068	0.088	0.0044	0.014	0.22	74.8	19.7	3.75
water glass 2.5:1	0.0005	0.0009	0.006	0.008	0.039	24.7	6.92	3.57
SWAN RIVER								
silica sand	0.005	<0.008	0.0083	<0.001	0.0115	>99.8	0.01	
fused glass	0.042	0.096	0.0066	0.027	0.62	75.3	20.8	3.62
water glass 2.5:1	0.0006	0.0008	0.008	0.004	0.118	22.6	6.51	3.47
fused glass INDUSTRY STANDARD								
low	0.032	0.004	0.005	0.004	0.15	75.36	23.21	3.24
high	0.17	0.10	0.030	0.052	0.51	76.0	23.89	3.18

Phase 2 - Melting Tests

A demonstration of the melt fusion process to produce an industrially acceptable sodium silicate was undertaken. To obtain a theoretical weight ratio of 3.22 SiO_2/Na_2O in the fused product the raw materials were incorporated into the silicon carbide crucibles at a mixture of 1005g silica sand samples and 535g soda ash. Two scoping tests performed in a platinum crucible on smaller samples determined CO_2 evolution temperature, foaming characteristics, and optimal molten flow temperature. The first scoping test (154g Illinois sand total) evolved the CO_2 at 900°C for 1 hour, then after holding the mixture for 30 minutes at each of 1000°C, 1100°C, 1200°C, 1300°C, and 3 hours at 1350°C, allowable flow was attained at 1350°C, The second scoping test with 307g raw material confirmed these observations. Analysis of the first scoping test solid glass product for sodium (9 mg Na/g) confirmed what subsequent first run Illinois solid glass analysis showed (158 mg Na/g) in that holding the temperature for 3 hours at 1350°C evolved Na as a volatile component. Although the crucible surface to volume ratio is different between the 2 aforementioned tests, a greater than 10 times difference in Na concentration of the 2 glass products is evident. As shown in Table 3, even at one hour of 1350°C fusion temperature, 18% to 28% Na from the 4 different melts potentially volatized away and indicates the need for tight process control.

Two runs of the Illinois standard and one run each of the Winnipeg and Swan River formations were performed, the results of which are presented in Table 2. While absolute mass quantification of the glass product is difficult due to laboratory test equipment limitations (eg. cooling crucible yielding poor flow), some qualitative observations are possible. Pouring the molten fused product into cold quench water resulted in a well fractured glass product of approximately minus 4 mesh. The clear unfractured residue on the cooled crucibles showed a slight brown tint to the Winnipeg and Swan River products and a white clear to the Illinois standard. Drying the wet product in pans at ~100°C resulted in some loss due to the tenaciously bound material. The quench water was sampled before and after glass quenching and did not contribute significant oxide values to the recovered solid glass product (Table 4).

Qualitative observations possible are selected percent oxides of the solid glass products. The $SiO_2:Na_2O$ ratios increased from a theoretical 3.22 to 3.26, 3.50, 3.62 and 3.75 (Table 2) and is assumed to be due to the previously noted Na volatility. Industry standards for impurity oxide levels in the solid sodium silicates, typically 3.3 $SiO_2:Na_2O$, were obtained from Kirk-Othmer (Encyclopedia Of Chemical Technology, Vol. 20, Wiley-Interscience Publication,1982). The aluminum concentrations in both the Swan River solid glass (oxide 0.62%) and liquid glass (626 ppm) are greater than the industry standards quoted (0.51% and 250 ppm). As a result of client provided external analysis on the raw materials (Swan River Al_2O_3~0.3%), these higher Al values may be associated with the increased Al_2O_3 value of the Swan River silica sand. All other oxide impurities are within or less than the guidelines suggested by Kirk-Othmer (1982).

Phase 3 - Silicate Dissolution

The planned dissolution ratio of 1 kg to 1 L water did not produce the expected results but did produce about 500 mL of 40 Beaume (specific gravity) water glass solution, which was prone to solidifying at room temperature. The remainder was a solidified mass on the impeller and autoclave sidewalls. Decreasing the above ratio to 1 part solid (Illinois), 3 parts water resulted in complete solubilization of the material as 1070 mL water glass, 30 Beaume (1.25 s.g.) with non-solidifying stability and metal values within the prescribed limits (Table 5). To produce a solution of higher specific gravity the solid:liquid ratio was decreased to 2.5:1. Tables 2, 5 and 6 detail the analytical results. Filtered volumes of water glass solutions were 1070 mL (Illinois 2.5:1), 1100 mL (Illinois 3:1), 1090 mL (Swan River), and 1100 mL (Winnipeg). All the filter cakes were ~1g and thus contributed insignificantly to the semi-quantitative balance (Table 6). In the production of the Swan River solution, a shorter autoclave residence time of 5.5 hours, as compared to 6 hours, resulted in ~50g of undissolved solid glass fused to the bottom of the titanium chamber. None of the analyzed elements needed for the client requested oxide parameters of the solutions were found to be in excess of the industry standards, except Al of the Swan River water glass as described previously. Of the 5 elements in excess of the industry standards, one (barium) was greater only in the Swan River sand (8.7ppm:2.8ppm). Three others, arsenic and phosphorous, just slightly greater than, and vanadium, 2-3 times as much, were higher than the standard in all the sands tested. Zinc was slightly greater than the standard and the Illinois water glass in both the Winnipeg sand (3.3 ppm:2.8 ppm) and the Swan River sand (5 ppm:2.8 ppm). Rationale for these five metal observations could not be made since the metals were not followed throughout the investigation. Brilliantly clear water glass solutions were the final result of this testwork, with specific gravities of 1.25 (Illinois 3:1), 1.275 (Illinois 2.5:1), 1.255 (Winnipeg) and 1.26 (Swan River).

Table 3
Solid glass and Na characteristics

	Illinois-1	Illinois-2	Winnipeg	Swan River
theoretical solids produced(g)	1317	1317	1317	1317
solids recovered (g)	1114	1205	1100	1150
solids loss (%)	15	9	16	13
theoretical Na loss (%)	3	1.5	3	2
theoretical product Na (g)	232	232	232	232
actual product Na (g)	176	188	160	177
total Na loss (%)	24	19	31	24
theoretical volatile Na loss(%) (total-theoretical Na loss)	21	17.5	28	22
time at 1350°C (hrs)	2	1.5	2	2
time at 900°C (hrs)	1	1.25	1	1.5

Table 4
Quench water oxides

	oxide weight %						
quench water	CaO	MgO	Fe_2O_3	TiO_2	Al_2O_3	SiO_2	Na_2O
before Illinois-1	0.006	0.0016	<10-5	<10-6	<10-5	0.0001	0.0022
before Illinois-2	0.0053	0.0016	<10-5	<10-6	<10-5	0.0002	0.0032
after Illinois-2	0.0007	0.0013	<10-5	<10-6	<10-5	0.0002	0.0032
before Winnipeg	0.0058	0.0016	<10-5	<10-6	<10-5	0.0001	0.0022
before Swan River	0.0038	0.0015	<10-5	<10-6	<10-5	0.0002	0.0043

Table 5
Experimentally produced water glass solution contaminants compared to 3.3 SiO_2:Na_2O industrial water glass

[metal]	Industry Standards		Illinois	Illinois	Winnipeg	Swan River
ppm	low	high	3:1	2.5:1	2.5:1	2.5:1
Al	50	250	232	251	207	626
As	<1	<1	<5	<5	<5	<5
Ba	<0.2	2.8	0.65	1.4	1.0	8.7
Ca	<1	76	3.9	2.7	3.8	4.5
Co	<0.3	<0.3	<0.1	<0.1	0.14	<0.1
Cr	<0.3	1.0	0.88	0.53	0.65	0.67
Cu	<0.6	1.1	<0.1	1.8	1.6	1.1
Fe	36	120	39	43	45	54
Mg	4	26	5.4	5.7	5.3	4.7
Mn	0.1	1.8	0.88	1.1	0.79	0.78
Ni	<0.3	<0.3	<0.1	<0.1	<0.1	<0.1
P	<18	<18	22	24	29	23
V	<0.3	<0.8	1.7	1.8	2.3	2.8
Zn	<0.6	2.8	0.62	0.86	3.3	5.0

Table 6
Insoluble filtered solid metal values from as-produced water glass solutions

	Insoluble Filtered Solids			
metal (ppm)	Illinois 3:1	Illinois 2.5:1	Winnipeg	Swan River
Al	4860	23000	2520	9240
As	790	570	580	33
Ba	<10	10	<10	<10
Ca	34700	20600	20000	10700
Co	80	13	12	15
Cr	120	510	53	130
Cu	300	74	22	120
Fe	1040	1940	490	1070
K	<100	<100	<100	1370
Mg	2220	1580	800	790
Mn	92	69	31	33
Na	26500	19200	33700	43400
Ni	120	570	98	240
P	<50	<50	<50	<50
Si	120000	84500	107000	216000
Ti	240	110	94	160
V	24	11	17	21
Zn	15	13	4.4	45

4. CONCLUSION

This testwork on two silica sand samples, Winnipeg and Swan River, has resulted in the production of both solid and liquid glass which are within the industry standards for the oxides of iron, calcium, magnesium, titanium and aluminum although the the Swan River sample showed a slightly higher aluminum oxide value in the fused glass solids, as well as an undissolved glass residue following the water glass production. A clear, bright water glass was produced using laboratory scale industrial methods which fell within the prescribed specific gravity range and SiO_2:Na_2O ratio. The industry standard sand, Illinois, was also used in the testwork for parallel comparison, and matched favourably to the tested parameters of the two experimental silica sands used. The completed testwork was based on the evaluation of typical sodium silicate production in the chemical manufacturing industry. Because of project budgetary considerations, the qualitative aspects of the process were deemed more important than exacting quantitative analytical measurements. By incorporating known analytical standards, or a more vigorous fusion technique for solids analysis, a precise mass balance would have been possible. Given the allowable product impurity levels and the relatively parallel qualities between the three glasses made, this project has shown that further investigations into the industrial processing of the Winnipeg and Swan River silica sand formations is warranted.

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