## PROCESSING GLASS GRADE SAND FROM DUNE SAND

by

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#### **ABSTRACT**

Naturally occurring sand deposits in the Southeast can only be used for glass making after special processing to meet stringent specifications of flat glass and container glass manufacturing companies. The North Carolina State University Minerals Research Laboratory assisted different glass sand producers with property evaluation and process development in batch and pilot plant to obtain parameters for reliable glass sand production from local deposits. The North Carolina State University Minerals Research Laboratory also assisted with flotation plant start-up and quality control problems. The glass sand specifications for the largest flat glass plant in the world, Libbey-Owens-Ford in Laurinburg, North Carolina, which uses the Pilkington float glass process, are now based on performance standards established by the first glass sand flotation plant in North Carolina at Marston, North Carolina. Carolina Silica, Inc., employs reliable mining, sizing, grinding, feed preparation, flotation, filtering, drying, and quality control procedures to supply the fast expanding glass sand industry in the Southeast with glass sand of extremely high quality.

Presented at Fourth Industrial Minerals International Congress in Atlanta, May 27-80, 1980

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#### INTRODUCTION

Modern society is highly dependent upon glass in its three basic forms:

(a) Container Glass, (b) Flat Glass, and (c) Fiberglass. Glass is the only material which can be produced upon the planet Earth without concern for exhausting the necessary resources. In its most basic form, glass can be produced from four primary constituents: (a) silica sand, (b) high-calcium limestone, (c) dolomitic limestone, and (d) soda ash. The first three constituents are naturally occurring raw materials which exist in abundance around the globe. The fourth, soda ash, exists as the mineral trona in the Western Desert areas of the United States, and to a more limited extent in Africa and Asia. Soda ash may also be produced from sodium chloride and coal using the Solvay Process.

The Glass Industry is comprised of three major divisions:

- A. <u>Glass Containers</u>: Container companies specialize in the production of bottles, jars, drinking glasses, television tubes and similar items. Major container companies within the United States include Owens-Illinois, Anchor-Hocking, Brockway Glass, Corning Glass Works, and Ball Brothers.
- B. <u>Flat Glass</u>: This glass is produced in a continuous flat ribbon. It has high-quality optical properties and is used for windows, curtain walls, automotive glass, mirrors, and similar products.

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Typical American companies include: PPG Industries, Libbey-Owens-Ford, and the Ford Motor Company.

C. <u>Fiberglass</u>: Fiberglass is glass extruded as mono-filament fibers. These fibers possess great tensile strength. This property has led to their use in automotive tire construction and such things as fiberglass boat hulls. Fiberglass is also in great demand for insulating purposes. Producers operating in the United States include: Owens-Corning Fiberglas, PPG Fiberglass, and Johns-Manville Corporation.

These three glass divisions -- Container, Flat Glass, and Fiberglass -- each utilizes a glass formulation tailored to yield specific physical advantages for its particular process. However, they do share one factor very much in common: all three are predominantly silica in composition, and this silica comes from sand.

Within the United States, a significant portion of the American Glass Industry is now located in the South Atlantic Region encompassed by the states of North Carolina, South Carolina, Tennessee, Mississippi, Georgia, Alabama, and Florida. Within this region, some 32 glass plants produce either glass containers, flat glass, or fiberglass (See Figure 1).

Prior to 1975, relatively little high-quality glass sand was produced within this area. Most of the high-quality sand required was shipped from processing plants sited along the well-known St. Peters (Early Ordovician) and Oriskany (Early Devonian) Formations. Both of these deposits are naturally low in heavy mineral content. Moreover, the refractory mineral particles within their respective heavy mineral arrays tend to be minus 0.15 mm (US No. 100 sieve)

in their least dimension. These sands have the advantage of requiring only relatively simple processing such as crushing, washing, drying, and sizing. On the other hand, they have the distinct disadvantage of long shipping distances into the Southeastern States. Rail shipping distances range from 1,000 to 1,500 kilometers, and freight costs run from 200 to 400% of the sand cost.

In 1972, Libbey-Owens-Ford announced plans to locate the world's largest glass furnace at Laurinburg, North Carolina. This plant was designed to produce flat glass using the Pilkington Process. Concurrently, efforts were initiated by Libbey-Owens-Ford to locate suitable raw materials in the required tonnages. 7,3 Top priority was given to locating glass grade sand. At that time, the nearest source capable of meeting LOF's technical specification was located at Guion, Arkansas, in the St. Peters Formation. This source was about 1100 kilometers by rail from the new plant and entailed a very severe transportation penalty.

Laurinburg is located about midway between Charlotte and Wilmington, North Carolina and is near the Fall Zone sand deposits which constitute the Sand Hills of North Carolina. The origin and age of these unconsolidated materials are not exactly known but generally are interpreted as dune sand of Post-Cretaceous Age. These deposits had long been recognized by geologists as being quite extensive. Some technical work had been carried out earlier by the North Carolina State University's Minerals Research Laboratory on beneficiating these sands to meet first-grade glass sand specifications. 6

The challenge of 1972-1974 was to establish a viable production facility in the Sand Hills capable of supplying Libbey-Owens-Ford's new plant at Laurinburg. Existing glass sand companies doubted that the technical limits set on the Residual Heavy Mineral Content by LOF could be met by existing process technology. However, a newly established glass sand company, known as Carolina Silica, Inc., met this challenge. The company was given substantial

Laboratory at Asheville through both batch and pilot plant research. In addition, Libbey-Owens-Ford's Technical Center, Toledo, Ohio, assisted through critical product evaluation activities and with glass-batch-material processing engineers assigned to work directly at Carolina Silica. As a result, in mid-1975 Carolina Silica established a uniquely successful glass plant at Marston, North Carolina, about 8 kilometers northeast of Rockingham, North Carolina. At this time, Carolina Silica is supplying the total sand requirements for both the original furnace at Laurinburg along with a second similar float furnace which became operational in March of this year. The great bulk of the sand shipped to LOF exceeds their quality standards by substantial margins. It is, by a wide margin, the highest quality glass sand being produced anywhere in the world.

### THE SAND DEPOSITS IN THE SANDHILLS OF NORTH CAROLINA

The Sand Hills area in the south central part of North Carolina is the most important source of silica sand in the State, with good accessibility to markets by rail and highway. Other deposits of less importance are the bay sands and costal sands of North Carolina. The 50-mile wide Sand Hills zone stretches from eastern Cumberland County through Moore, Hoke, Scotland, Richmond and Anson Counties, westwards into South Carolina. The unconsolidated deposit ranges in thickness from 2 to 15 meters and consists of relatively clear, crystalline, subangular quartz sand with low clay and gravel content. The principal impurities are clay and mica, along with heavy minerals including kyanite, zircon, sillimanite, andalusite, leucoxene, rutile, tourmaline, hematite, magnetite and limonite. The content of minerals having a specific gravity of 2.96 or greater averages about 1%. Up to 20% of this heavy mineral content can be refractory heavy minerals, detrimental to glass production,

especially if larger than 0.210 mm (US No. 70 sieve). The median size distribution of the sand is about 0.300 mm (US No. 50 sieve) with some 40% retained on a US No. 40 sieve (0.4 mm). Most American container and flat glass companies prefer sands with no more than 10% retained on a US No. 40 sieve. This means about 30% of the sand is coarser than the glass industry usually accepts and must be removed or comminuted to size specifications.

Typical chemical and mesh analyses for raw Sand Hills sand are presented in Table 1.

TABLE 1
RAW SAND HILLS SAND

#### Typical Chemical Analysis

Constituent	Symbol	Percent Present
Silica	SiO <sub>2</sub>	97.1
Total Iron	Fe <sub>2</sub> 0 <sub>3</sub>	0.25
Alumina	A1203	1.8
Calcia + Magnesia	CaO + MgO	0.06
Loss on Ignition	LOI	0.67

#### Typical Screen Analysis

US Standard Sieve	Opening mm	Percent <u>Retained</u>	Cum. Percent Retained
20	0.85	9.4	9.4
30	0.600	15.6	25.0
40	0.425	22.4	47.4
50	0.300	20.5	67.9
60	0.250	7.5	75.4
80	0.180	10.1	85.5
100	0.150	7.5	93.0
140	0.106	1.6	94.6
-140		5.4	100.0

The nature of the Sand Hills deposits so defines the processing problems: (a) first size and grind to specifications; and (b) remove detrimental impurities by special processing.

#### TECHNICAL CRITERIA FOR GLASS SAND

Silica sand constitutes about 60% of the raw batch composition used by most Container and Flat Glass producers. As sand is the major constituent, quality of the sand is a primary factor in determining quality of the finished glass. There are three basic parameters which affect the "Technical Acceptability"\* of any sand under consideration for use in glass batch:

- Chemical Composition
- 2) Size Distribution
- 3) Trace Contaminant Levels

#### Chemical Composition

The key to production of high-quality glass lies in the exercise of precise control over the glass composition entering the melting furnace. Many physical properties of glass are extremely sensitive to very slight changes in formulation. Even minor fluctuations in composition of the glass melt can, and do, cause serious quality problems, and adversely affect production operations. For these reasons, a modern glass plant is designed to exercise an exacting level of control over its glass composition.

Chemical control of the glass commences with chemical control of the raw materials. Each raw material entering the glass batch must have a high level of chemical uniformity, minute to minute, hour to hour, day to day, and month to month. Chemical uniformity is the number one quality factor in the evaluation of any glass-making raw material. For glass sand, there must be un-

<sup>\*</sup>Libbey-Owens-Ford terminology

qualified assurance that, each time a ton of sand is weighed into the batch, it will yield the same number of pounds of silica, alumina, and iron. There must be no surprises.

It may sound trite, but it is important to recognize that sand is purchased for its silica content. Anything else in the sand may be regarded as a contaminant. The level of the silica -- that is, the  $\mathrm{SiO}_2$  -- is not overriding. Most high-quality glass sands exceed 99.5%  $\mathrm{SiO}_2$  when processed for shipment, and many will average close to the 99.80% level. However, the silica in the sand is not the problem; rather, it is that fraction which is not silica. The non-silica fraction will include the clays and a host of minerals which contribute iron, aluminum, titanium, calcium, magnesium, and various trace constituents. It is worthy of note that the Glass Industry usually totals all of the separate iron contributions within the sand, regardless of source, and considers it as a single value in terms of  $\mathrm{Fe}_2\mathrm{O}_3$ . In a like manner, all aluminum contributions are reported as a single value in terms of  $\mathrm{Al}_2\mathrm{O}_3$ ; the same treatment is applied to any other cations which may be present.

Three of the primary materials entering glass batch -- sand, dolomite, and high-calcium limestone -- are products of nature. Even with advanced processing techniques, some variances will occur. For our purpose, "Variance" may be defined as the arithmetical difference between the highest and lowest analytical values, as acquired over a span of several months. The term "Range" may be used synonymously for "Variance". For sand, the amounts of variance which can usually be accepted, are presented in Table 2.

TABLE 2
ACCEPTABLE VARIANCE

Constituent	<u>Symbol</u>	<u>Range</u>
Silica	SiO <sub>2</sub>	0.15% Max.
Total Iron	Fe <sub>2</sub> 0 <sub>3</sub>	0.010% Max.
Alumina	Al <sub>2</sub> 0 <sub>3</sub>	0.07% Max.
Calcia	Ca0	0.025% Max.
Magnesia	MgO	0.025% Max.

It has been brought out that any constituent in the glass sand, other than silica, must be considered as a contaminant. The principal contaminants include: iron, alumina, and titania. Other contaminants may be present in lesser amounts, down to trace levels. Residual moisture is also a contaminant, since it may cause the silica level to vary. Some constituents, such as alumina and moisture, affect glass composition. Others are powerful colorant agents. The tolerance levels for specific contaminants may vary somewhat according to the end use of the glass. However, most glass operations can accept sand with contaminants up to the levels presented in Table 3.

TABLE 3
CRITICAL CONTROL LIMITS

Constiuent	<u>Symbol</u>	<u>Limit</u>
Total Iron	Fe <sub>2</sub> 0 <sub>3</sub>	0.025% Max.
Alumina	A1 <sub>2</sub> 0 <sub>3</sub>	0.200% Max,
Titania	Ti0 <sub>2</sub>	0.03% Max.
Calcia	CaO	0.05% Max.
Magnesia	Mg0	0.05% Max.
Chromium	Cr <sub>2</sub> 03	0.0002% Max.
Cobalt	Co <sub>3</sub> 0 <sub>4</sub>	0.0002% Max.
Manganese	Mn0 <sub>2</sub>	0.0020% Max.
Moisture	H <sub>2</sub> 0	0.05% Max.
Loss on Ignition*	LOI	0.12% Max.

<sup>\*</sup>Includes moisure

#### Size Distribution

In the not too distant past, glass-making personnel were prone to blame a host of operational problems on the mesh of the sand in use. It was too fine, too coarse, too this, or too that. Rapid advances in glass technology during the fifties and early sixties served to dispel most of these myths. Major glass companies, in both the container and flat glass fields, recognize that large production furnaces are not temperamental about sand mesh. This has been of great benefit to the glass sand industry. Each producer can concentrate on one or two mesh grades, predicated upon the natural mesh distribution of his own particular deposit.

There need be only two mesh control points for glass sand -- one at the coarse end and another at the fine end.

- A. <u>Coarse End</u> The sand should be essentially minus 0.425 mm (US No. 40 sieve).
- B. <u>Fine End</u> The sand should be essentially plus 0.106 mm (US No. 140 sieve).

Notice that each control point includes the word: "essentially". It is not said that <u>None</u> of the sand may be larger in size than 0.425 mm (US No. 40), nor that <u>None</u> may be finer than 0.106 mm (US No. 140). Rather, the intent is that most of the sand lies between these two screen sizes. Almost all American glass sands have 85% or more of their total weight within this range. It is important, however, that any given sand <u>establish</u> and <u>hold</u> a reasonably consistent mesh distribution on the intermediate screens between US No. 40 and US No. 140.

Glass sand does have some critical mesh control points above the US No. 40 and below the US No. 140. These are presented in Table 4.

TABLE 4
ACCEPTABLE SIEVE SPECIFICATION

Requirement	Opening, mm	Sieve Size, US Standard	<u>Limits</u>
Cum. Retained On:	1.18 mm	No. 16	Not one piece
Cum. Retained On:	0.85 mm	No. 20	0.01% Max.
Cum. Retained On:	0.425	No. 40	0.10% Max.*
Cum. Retained On:	0.106	No. 140	92.0 % Min.
Cum. Retained On:	0.075	No. 200	99.5 % Min.
Cum. Retained On:	0.045	No. 325	100.0 % Min.

<sup>\*</sup>May be substantially modified if the base deposit is substantially free of refractory particles exceeding US No. 70 (0.212 mm).

A large particle of silica may be considered as a refractory-type contaminant, since it may fail to melt compeltely during its pass through the furnace. The maximum-size particle which can be assuredly melted, will vary with the design of the individual melting furnace, the firing temperatures employed, and the rate of batch fill. For these reasons, glass companies prefer to keep the top particle size within a "sure-safe" melting range. Almost all American Container and Flat Glass Companies set this point at US No. 20, equivalent to a particle diameter of 0.85 mm. An absolute cut-off point is maintained by Libbey-Owens-Ford at US No. 16 or 1.18 mm.

The US 40 sieve limit is controlled chiefly by the mineralogy of the base deposit. Every sand source which Libbey-Owens-Ford has investigated contains some finite amount of refractory mineral particles. In a few, such as the St. Peter Formation, all of the refractory particles are sufficiently small in least dimension to present very little or no threat. In other deposits, however, larger particles of refractory minerals may be quite common. These must not get into the furnace. The only sure-safe guarantee against these particles is to require that all of the sand be minus US No. 40. Where large refractory particles are not a threat, the sand may include up to 12-15% plus US No. 40 material.

On the fine end of the spectrum, concern relates chiefly to the health hazards associated with fine silica, and the air quality standards imposed by the United States Environmental Protection Agency. Basically, that fraction finer than US No. 140 should be minimized. There must be no material finer than US No. 325 since such particles may remain airborne for a considerable length of time. In a practical sense this need not be a problem since most of the sub-fines are removed in the wash operations as slimes.

#### Trace-Contaminant Levels

Certain trace contaminants can very seriously affect glass quality and make it unacceptable for various critical applications. Such contaminants may be objectionable as <u>either individual particles</u> or as <u>minute percentages</u>. These contaminants fall into three basic categories:

A. <u>Colorants</u> - Minerals composed of cobalt, chromium, manganese or nickel salts are very potent colorants and may seriously affect color of the glass and its light transmission characteristics. Limits on these colorants were presented under "Critical Control Limits" in Table 3.

- B. <u>Metallic Particles</u> Individual particles of aluminum, copper, brass and bronze are objectionable and must be excluded from the finished sand. This requires severe restrictions upon the use of these metals in the process systems.
- C. Refractory Particulates Certain heavy minerals of a refractory nature resist solution in the molten glass during the glass melting process. Such particles can be the direct cause of very severe production losses. A refractory heavy mineral particle is defined by Libbey-Owens-Ford as a discrete particle having a specific gravity of 2.96 or greater; and such particle, having a size of 0.425 mm (US No. 40) in least dimension, fails to fully melt out and disperse within a matrix of soda-lime glass when heated at a temperature of 2400° F for 60 minutes. Typical refractory minerals meeting this definition include:

*Chromite	FeCr <sub>2</sub> 0 <sub>4</sub>	Andalusite	A12Si05
Corundum	A1 <sub>2</sub> 0 <sub>3</sub>	Kyanite	Al <sub>2</sub> Si0 <sub>5</sub>
Zircon	ZrSiO <sub>4</sub>	Sillimanite	A1 <sub>2</sub> Si0 <sub>5</sub>
Zirconia	ZrO <sub>2</sub>	*Other Spinels	

All of the principal sand formations in the southeastern United States are known to carry some or all of these refractory heavy minerals. Glass technology researchers at Libbey-Owens-Ford have developed solution rate curves for kyanite, corundum, and zircon in soda-lime glass melts. For kyanite, the rate of solution was found to be 0.017 lineal inches per hour at 2600° F.\*\*
For corundum, the rate was 0.007 inches per hour, and for zircon 0.006 inches per hour. 3,4 (See Figure 2)

<sup>\*\*</sup>Overall average glass melt temperature in a production furnace.

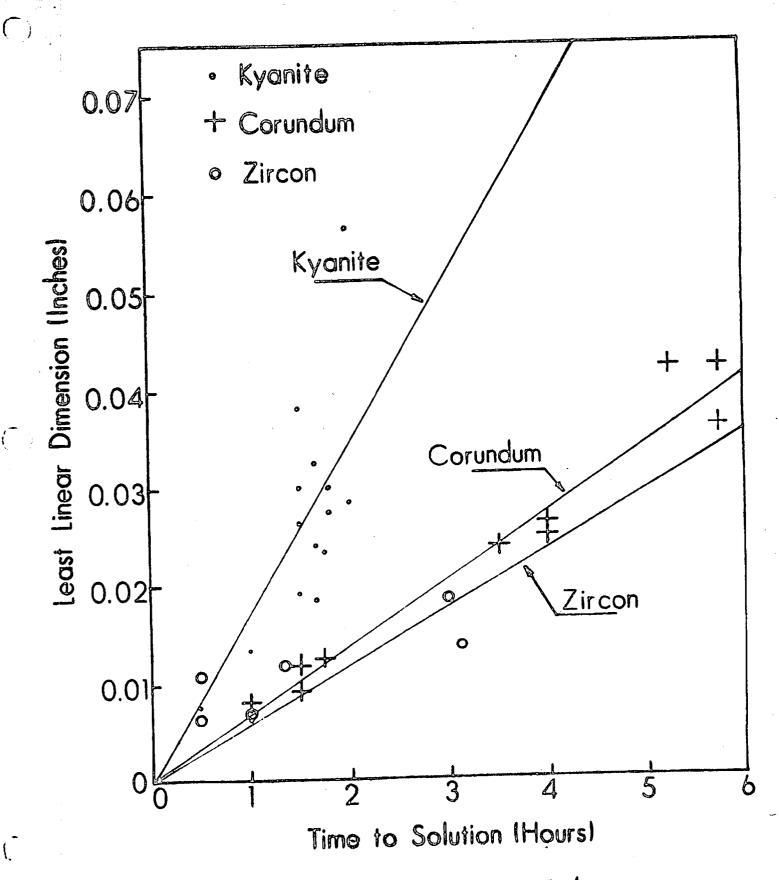


Fig. 2. Initial Particle Size vs. Time to Solution

Such experimental work, coupled with analyses of on-going operations, has led Libbey-Owens-Ford to the conclusion that refractory particles with the least dimension less than 0.212 mm (US No. 70 sieve size) will melt out with a high level of confidence. Particles larger than 0.212 mm (US No. 70 sieve) in least dimension present increasing levels of uncertainty. In a general context, any refractory particle may be expected to contribute a glass defect (stone, cord, etc.) when its initial size exceeds 0.425 mm (US No. 40) in its least dimension. Based upon the foregoing, Libbey-Owens-Ford has established the following specification limits on refractory heavy minerals for finished glass sand:

TABLE 5
TOTAL REFRACTORIES SPECIFICATION

Requirement	Opening, mm	Sieve Size, US Standard	Grams per 100 lbs Product
Cum. Retained On:	*0.425 mm	No. 40	Not one piece
Cum. Retained On:	*0.212 mm	No. 70	**0.200 grams cum. max.

<sup>\*</sup>As received basis

These refractory specifications translate into the following:

Basis	Minus US No. 40 Plus US No. 70
Weight Percent	0.00044 %
Per 100 Lbs Sand	0.200 Grams
Per 100-Ton Rail Carload	400.0 Grams

The chemical composition is determined by classical analytical techniques applied by individual glass and glass sand companies to the specific requirements. The size distribution is determined by standard testing sieves and screening methods. The trace contaminants are determined as the specific case requires. The heavy mineral content is determined by separation of samples in tetrabromoethane (sp gr 2.96), and refractory properties by examination of sink products

<sup>\*\*</sup>All refractories combined

by microscopy before and after dissolution in a glass melt, supplemented by x-ray diffraction where necessary.

#### GLASS SAND PRODUCTION FROM DUNE SANDS

#### Mining

The unconsolidated sand deposits in the southeast are generally mined above water table by dry excavation with front-end loaders or power scrapers, and below the water table by underwater excavation with dredges or cable-operated draglines or scrapers. Trucks transport the dry, raw sand to trash trommel screens and slurrying sumps for pipeline transport, while dredges can pump the sand directly to the trash screens and process plants. Usually plus 6 mm coarse material or organic trash is removed by trommel screens before a primary desliming and dewatering step followed by stockpiling, or before direct pipeline transport into the processing plant.

#### Feed Size Preparation and Clay Removal

The slurried sands are pumped to primary desliming where hydrocyclones or screw classifiers remove minus 0.1 mm primary slimes. The slimes, containing mainly clay minerals and some fine quartz sand, are settled in ponds; subsequently this water is recirculated as process water. After primary desliming, the sands are sized, either by hydrosizing in free- or hindered-settling tanks, or on screens, or by a combination of both, to remove the coarser fraction - usually plus 0.5 mm. This coarse fraction may be stock-piled and sold to non-glass-sand users or comminuted by grinding in ball mills to minus 0.5 mm for glass sand processing. The hydrosized minus 0.5 mm sand is dewatered in screw classifiers, or a combination of hydrocyclones and screw classifiers, to 70 to 80% solids for attrition scrubbing.

Attrition scrubbing is carried out in multiple-compartment, propeller-

type scrubbers. Wemco and/or Denver-type machines are preferred by the glass sand industry. Attrition scrubbing loosens and disperses coatings of iron oxides, clay minerals, and other cementing and flotation-affecting materials from the sand grain surfaces. Attrition scrubbing also prepares fresh surfaces on the detrimental non-quartz minerals for reagent attachment in the following flotation conditioning step. Two stages of attrition scrubbing, each followed by desliming at 0.1 mm in cyclones or screw classifiers, are recommended for reliable flotation feed preparation. Attrition scrubbing is normally done at high solids (70-80% solids). It is also a practice to add sodium hydroxide at rates of 500 to 1000 grams per metric ton of sand. The retention time in multiple-compartment-type scrubbers usually ranges between 3 and 15 minutes, and the power requirements vary from one to six kw-hr per metric ton of feed.

The oversize removed in the hydrosizing or screening step prior to scrubbing can be ground by steel ball milling to essentially minus 0.5 mm and recirculated to the sizing section. Steel ball milling of the coarse fraction of sand from the North Carolina Sand Hills actually reduces the heavy mineral content in the coarse fraction by differential grinding, and thus contributes to efficient removal of detrimental heavy minerals in the flotation step. A reduction in the upper size of the glass sand from about 0.5 mm to about 0.25 mm, without an increase in the amount of minus 0.1 mm fines, should result in energy savings and increased furnace throughput for the glass plants. Continuous pilot plant test work to demonstrate steel ball milling, hydrosizing and heavy-mineral flotation was conducted at the North Carolina State Minerals Research Laboratory in Asheville by request of both glass companies and glass sand producers. This confirmed the very encouraging results of earlier batch test work. 11

#### Removal of Detrimental Minerals by Flotation

After intensive investigation of anionic and cationic flotation techniques to either float the clean sand from the impurities or to float the impurities away from the glass sand product, and after investigation of gravity, magnetic and electrostatic separation methods, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21 it was determined that the anionic flotation removal of impurities from the sand, using petroleum sulfonate collector in an acid circuit, would reliably recover high-quality glass sand with minimum losses. A relatively simple single-stage flotation step could reduce the total heavy mineral content from 0.5 to 1.0% in the prepared flotation feed to less than 0.0005 to 0.0008% in the final glass sand, with an efficiency of heavy mineral removal of over 99.9%. It is very relevant to note that over 90% of the total glass sand tonnage delivered to the Libbey-Owens-Ford Laurinburg plant by Carolina Silica during the period 1975-1980 has had a total residual heavy mineral level of less than 0.10 grams per 100 pounds of finished sand. This is far better performance than required by Libbey-Owens-Ford's refractory specification presented in Table 5. The key to such success is good flotation feed preparation by attritioning and desliming followed by intensive conditioning at low pH with petroleum sulfonate, and froth flotation of heavy minerals using a glycol-type or alcoholtype frother to separate the heavies from the sand. 22,23 Intensive conditioning in propellor-type acid-resistant conditioners is done at plus 55% solids, with retention times of 5 to 15 minutes, using at least three conditioners in series to prevent short-circuiting. The petroleum sulfonate collectors are complex (Aerofloat 800 series by American mono sodium salts of alkylaryl hydrocarbons Cyanamid Company or Morco 62 or 70 series by Marathon Morco Company). 23,24 Petroleum sulfonates are oil and water soluble byproducts from white mineral oil refining by reaction with 20% oleum. Mono sodium sulfonates have fairly

long hydrocarbon chains and have the following approximate formula:  $CH_3(CH_2)n - C_6H_6-SO_3-Na$ , with the number of carbon atoms(n) being larger than 20. The anionic petroleum sulfonate collectors hydrolize at pH values below 2.0 into very active negatively-charged polar hydrocarbons with affinity to positively-charged ions found on the surfaces of the heavy minerals. The hydrocarbon chain of the collector renders the mineral surfaces hydrophobic or water repellent; therefore, they have affinity to the air bubbles in the flotation pulp and are lifted to the surface and removed in the froth. The petroleum sulfonate collector is strongly absorbed and firmly held on the surfaces of the heavy minerals. The low pH value also enhances the negative surface charge of the attrition-cleaned quartz sand, which prevents attachment of collector. Sulfuric acid is used for pH adjustment in the conditioner. The flotation separation is accomplished in impeller-type, supercharged, acid-resistant flotation machines in open-trough arrangements of 5 or 6 cells. Denver DR-type flotation machines or Wemco machines are in use in the Southeast. 25,26 The flotation density is held at around 30 to 33% solids, and the retention time in the flotation cells is around 8 to 15 minutes. It is of utmost importance to keep the froth level in the flotation machine constant and at a high optimum level at all times, which is accomplished by use of automatic level control and careful supervision of the flotation process. Most of the heavy minerals are removed in the froth of the first 3 to 4 flotation cells, and the remaining cells are a safety precaution to guarantee complete removal at all times. The heavy mineral froth material is usually wasted since it is a relatively minor amount of many different minerals; some of them, such as rutile, ilmenite, etc., could have value if found in large enough quantities.

#### Drying, Shipping and Quality Control

The flotation cell underflow discharge, the glass sand product, is dewatered in cyclones to about 60 to 70% solids and then filtered on vacuum belt filters or horizontal table filters to about 6 to 7% moisture. The water from cyclones and filters is recirculated to the flotation cells as makeup water. The filtered sand must be further dried to less than 0.1% moisture. Drying is normally done in rotary or fluid-bed-type dryers, with wet scrubbers on the exhaust system. The Starnell fluid-bed-type dryers, made by Roberts and Schaeffer Resource Service Inc., are used by many glass sand producers because of high reliability and good thermal efficiency. Fuel consumption averages 1.5 to 2.0 gallons of #2 fuel oil per metric ton of sand. Pollution control on the dryers is usually by wet scrubbing of the exhaust gases. The hot scrubber water is returned to the filter and contributes to lowering of moisture content by 1 to 2%. The dried sand is conveyed to check screens for final size control and is sampled and stored in silos for shipment either by rail or by truck. In order to guarantee uniformity of glass sand product. all conditions in the processing plant, such as feed rate, water addition. reagent additions, and percent solids in scrubbing, conditioning and flotation cells, have to be kept within narrow established limits. The quality of glass sand produced in the flotation plant is monitored continuously by quality control personnel, and provisions are made to reject off-grade sand before it enters the product silo. Operating personnel of the sand companies are trained to adhere strictly to established procedures and to take fast corrective actions when needed. In order to assure uniform quality of glass sand for Libbey-Owens-Ford's Laurinburg float glass plant, every truckload is sampled at the time of loading and is released for dumping into the glass plant silo only after size analysis and heavy mineral determinations confirm that quality requirements are met.

#### Water Recirculation and Conservation

The quantity of process water used for glass sand processing is in the order of 10 to 20 tons of water per ton of glass sand. The largest amount of water is used for pipeline transport, washing, sizing, scrubbing and desliming. The flotation process uses only around 3 tons of water per ton of sand. With exception of the moisture loss in the drying process, all water can be recirculated through a pond system, where clay slime and other wasted material settles out and clear water can be reclaimed. Seepage and other water losses have to be made up with fresh water pumped by deep wells from the aquifer or from surface streams. The fresh water is preferably used in the last desliming step and as makeup water in the flotation cells. The sulfuric acid used in conditioning and flotation is neutralized by the sodium hydroxide in the scrubbing and desliming steps, and the pond pH can be kept around neutral. A schematic flowsheet of a plant to process glass grade sand from dune sands in the Southeast is presented in Figure 3.

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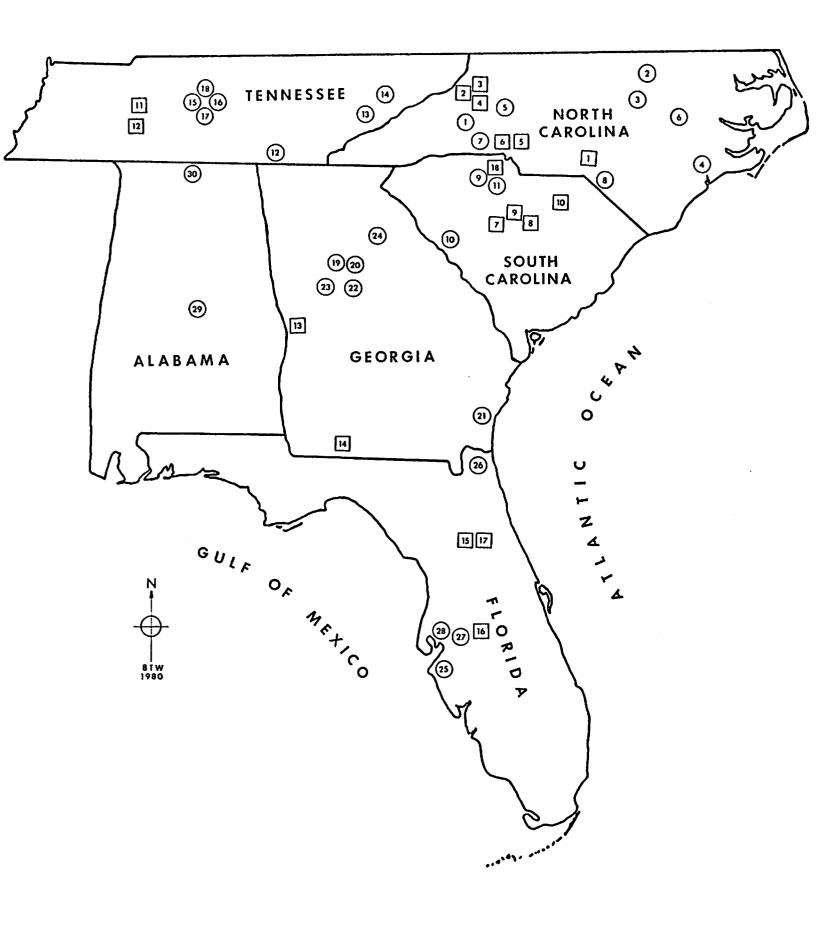


FIGURE 1. GLASS PLANTS AND GLASS SAND PRODUCERS IN SOUTHEASTERN USA

### Nr)

#### GLASS PLANTS IN SOUTHEASTERN USA

- 1. Ball Brothers Corporation (Containers)
  Asheville, North Carolina
- 2. Laurens Glass Company (Containers) Henderson, North Carolina
- 3. Corning Glass Works (Containers) Raleigh, North Carolina
- 4. Corning Glass Works (Containers) Wilmington, North Carolina
- 5. Owens-Illinois, Inc. (Containers)
  Winston-Salem, North Carolina
- 6. Kerr Glass Manufacturing Company (Containers) Wilson, North Carolina
- 7. Pittsburgh-Plate-Glass-Company (Fiberglass) Shelby, North Carolina
- 8. Libbey-Owens-Ford Company (Flat glass)
  Laurinburg, North Carolina
- 9. Laurens Glass Company (Containers)
  Laurens, South Carolina
- 10. Owens-Corning Glass Company (Fiberglass)
  Aiken, South Carolina
- 11. Owens-Corning Glass Company (Fiberglass)
  Anderson, South Carolina
- 12. Chattanooga Glass Company (Containers) Chattanooga, Tennessee
- 13. ASG Industries, Inc. (Flat glass)
  Greenland, Tennessee
- 14. ASG Industries, Inc. (Flat glass)
  Kingsport, Tennessee
- 15. Ford Motor Company (Flat glass)
  Nashville, Tennessee
- 16. Reichhold Chemicals (Fiberglass)
  Nashville, Tennessee
- 17. Owens-Corning Glass Company (Fiberglass)
  Nashville, Tennessee

- 18. Ferro Corporation (Fiberglass)
  Nashville, Tennessee
- 19. Glass Containers, Inc. (Containers) Atlanta, Georgia
- 20. Owens-Illinois, Inc. (Containers)
  Atlanta, Georgia
- 21. Hanibal Scientific Corporation (Containers)
  Brunswick, Georgia
- 22. Midland Glass Corporation (Containers) Warren-Robbins, Georgia
- 23. Owens-Corning Glass Company (Fiberglass) Fairburn, Georgia
- 24. Certain-Teed Corporation (Fiberglass) Athens, Georgia
- 25. Industrial Glass Company (Containers)
  Bradenton, Florida
- 26. Anchor-Hocking Corporation (Containers)
  Jacksonville, Florida
- 27. Owens-Illinois, Inc. (Containers)
  Lakeland, Florida
- 28. Thatcher Glass Manufacturing (Containers) Tampa, Florida
- 29. Brockway Glass Company, Inc. (Containers)
  Montgomery, Alabama
- 30. Owens-Corning Glass Company (Fiberglass)
  Huntsville, Alabama

### FIGURE 1. LIST A (CONTINUED)

- Carolina Silica, Inc. Marston, North Carolina
- 2. IMC Chemical Group, Inc. Spruce Pine, North Carolina
- 3. The Feldspar Corporation Spruce Pine, North Carolina
- 4. INDUSMIN Lawson United Feldspar & Mineral Company Spruce Pine, North Carolina
- 5. Foote Mineral Company
  Kings Mountain, North Carolina
- 6. Kings Mountain Silica, Inc. Kings Mountain, North Carolina
- 7. Pennsylvania Glass Sand Company Edmund, South Carolina
- 8. Pennsylvania Glass Sand Company Cayce, South Carolina
- 9. Columbia Silica Sand Company Columbia, South Carolina
- 10. Martin Marietta, Wedron Division Lugoff, South Carolina
- 11. Hardy Sand Company Camden, Tennessee
- 12. Martin Marietta, Wedron Division Sewanee, Tennessee
- 13. Georgia Silica, Inc., Division of Jessie Moore Junction City, Georgia
- 14. Dawes Silica Company Thomasville, Georgia
- 15. The Feldspar Corporation, EPK Division Edgar, Florida
- 16. Standard Sand and Silica Company Davenport, Florida
- 17. Florida Rock Company Interlachen, Florida
- 18. Lithium Corporation of America, Spartan Minerals Division Pacolet, South Carolina