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Solubility of glass tank refractories using a small electrically heated furnace

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SOLUBILITY OF GLASS TANK REFRACTORIES USING A SMALL ELECTRICALLY HEATED FURNACE

By

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THESIS

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SOLUBILITY OF GLASS TANK REFRACTORIES

INTRODUCTION

In the past few years glass tank operation has been subjected to much serious study in regard to the all-important refractory lining of the tank. Economical and efficient operation of a glass tank will depend primarily upon the composition and the type of the refractory lining used. However, the composition of the glass batch, and furnace design and operation are important factors.

The destruction of refractories by melting glass is of a physical and a chemical nature. The melted glass first penetrates into the pores of the refractory and then promotes the occurance of pyrochemical reactions. The deterioration of refractories is by no means a result of simple reactions. The refractory is exposed at a high temperature to a molten silicate which is very active. The blocks also have to carry the weight of the upper part of the furnace and the crown of the tank, and in addition must resist the thrust of the molten glass. The resistance of the blocks to corrosion is influenced by such factors as mineral composition, porosity, uniformity and fineness of texture of the block, and the temperature of the furnace.

A knowledge of the comparative values of different types of refractories for use in glass tanks is of much interest to glass manufacturers, because the life of such furnaces depends on the life of the refractory lining.

PURPOSE OF INVESTIGATION

This investigation was undertaken to study the refractory blocks used in glass furnaces--their relation with the molten glass. It was decided to employ for this examination a model glass tank, heated by electrical carborundum resistors known as Globars.

Experimental glass tanks have been constructed[1] using fuel oil or gas to obtain the required heat to perform melting. These fuels were used mainly to simulate commercial practice and thus to obtain results which could be easily applied to industrial furnaces.

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[1]Grigsby, C.E., Glass Tank Model, Jour. Amer. Cer. Soc., 12, 241, (1929).

The design of a model electric tank is included as part of this investigation.

METHODS OF TESTING

At a meeting of the international Glass Congress, in July, 1936, Doctor Otto Bartsch[2] gave a discussion on the various methods used for testing of tank block refractory materials. It must be remembered that the testing method is very important, and should always be considered when interpreting the results of the experiment.

Three common methods of testing the effect of glass on refractory materials are: 1. Model tank method. 2. Immersed rod of refractory. 3. Floating Refractory method. The methods are of value as regards solution profile and surface corrosion.

According to Dr. Bartsch, the use of the model tank method of testing is perhaps the most useful and important method. There is, as yet, no generally accepted method or procedure for the testing of tank blocks.

The glass tank method permits the determination of the following properties, namely:

(a) The degree of attack, both in the plane of the

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[2] Bartsch, Dr. Otto, Testing of Tank Blocks, Jour. Soc. Glass Tech., <u>20</u>, 536, (1936).

glass level and on the surface attacked.

(b) The danger of stones, by information concerning the nature of the rough surface below and especially above the glass level.

(c) The homogeneous character of the brick, by the formation of local corrosion areas, holes and furrows.

(d) The sensitiveness to temperature change on heating up. Blocks which cannot stand thermal changes develop small cracks which are washed out during the test and thus increase corrosion above normal.

Furthermore, the tank method gives some idea of the properties technically important for a tank block with the exception of the danger of cord formation. This cannot be obtained, according to Bartsch, from the model tank method. Also, the estimation of the risk of stones is also, by this method, a matter of opinion, and a conclusion regarding the tendency to stone formation from the appearance of the surface is not reliable.

The real importance of this method is that it permits the determination of the insolubility of the block under conditions closely approximating actual practice. The solution behavior can be judged with safety only in regard to the appearance of the surface—smooth or irregular contour. Two disadvantages of this method are in the long, uninterrupted testing period, often lasting a month, and the relatively large apparatus needed.

While the usefulness of laboratory tests on a small scale cannot be denied, it is logical to assume that the testing of blocks by construction of a small tank is likely to furnish the most direct information of a practical nature. Although this method is expensive, both in time and money, it has been employed, notably in the United States and in Germany.

It is well established that graphite resistors should not be used except where air is excluded. However, industrial experience has shown that, when operated in an air-tight furnace, the atmosphere within becomes rapidly reducing and protects the resistors against oxidation or combustion.

Toward 1934[3], the Plate Glass Works of Saint Gobain, used to fuse quartz, a small rotating furnace having a carbon resistor arranged along the axis of the apparatus and radiating freely upon the charge to be melted.

In 1934[4], the Society of Brown-Boveri applied electrical heating by radiation to a small tank furnace having a melting chamber communicating through a throat with the

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3 Devillers, R.W., & F.E. Valerwyck, Glass Tank Furnaces, Edited by S.R. Scholes, Ogden-Watney, Inc., 1937, p.8.

4 Ibid.

refining compartment. The heating elements ran through the space above the bath in both compartments in a plane parallel to the level of the glass and about 12 inches from it.

In 1935, Bivort[5] applied electrical heating on a semi-industrial scale to a small furnace for glass melting, arranging the heating elements in the crown of the device quite close to the glass bath. The carborundum resistors were from 3 to 5 feet long. Their normal life was from 2,500 to 3,000 hours. The first results were very satisfactory, and industrial applications of the process seemed to be about realized.

Some early tanks were constructed with standard size brick. Grigsby[6] used a tank of this type and rotated it while partly filled with molten glass. The decrease in volume of the bricks gave a measure of the attack experienced by the brick. It was found that the physical structure of the refractory was a very important feature in determining the degree of corrosion.

The U. S. Bureau of Standards made a laboratory investigation on commercial tank blocks. This test was reported by Pendergast and Insley[7]. For this test an experi-

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[5]*Ibid*, p. 7.

[6]Grigsby, C. E., *op. cit.*, p. 4.

mental gas-fired, continuous design was used. The construction was such that the blocks could be easily removed. In its final form the furnace was a modified down-draft kiln, the gases burning while they passed horizontally over the tank. Two burner ports were provided, with the fuel being water gas. The tank was 12 inches high, 12 inches wide, and 48 inches long, with the glass level 2 inches from the top of the blocks. The crown was of silica brick, and the bottom blocks and tuck stones were made of a modified glass-pot body developed at the Bureau of Standards, and composed of 50% firebrick grog fired to cone 16, and 50% of unfired Tennessee and Kentucky Ball clay and North Carolina kaolin. Nine melts were run, using various refractories, each test running about 30 days.

Batch fills at 12.5 pounds each were made each 15 minutes during eight consecutive hours. The batch was composed of 1,000 lb. of sand, 700 lb. soda ash, 200 lb. limestone, and 2 lb. sodium nitrate. One part cullet was mixed with three parts of raw batch. From 9,000 to 13,000 pounds of corrosive glass were melted in each 30-day period, at temperatures ranging from 1,425 to 1,525°F. The results showed that the rate of glass movement was sufficient to give marked corrosion with most refractory

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[7]Pendergast, W.L., & H. Insley, The Service of Refractory Blocks In Small Experimental Tank, U.S. Bureau Stds., 2, 453, (1929).

blocks at the end of a 30 day melting time. The calculated chemical composition of the batch was 66.3% SiO_2, 26.8% Na_2O, 4.0% CaO, and 2.9% MgO. This batch was higher than the average soda-lime bottle glass batch in soda and therefore more corrosive. The temperature measurement was by use of an optical pyrometer sighted at the center of the arch. In one run four Pt, Pt-Rh thermocouples were inserted in holes in the side-wall blocks. A difference of about 50°F. between the couples at the bottom and the top of the glass in the same vertical line was reported.

Comparison between the different blocks built into the same tank was not possible because they were not all exposed to the same corrosive action. Little relation was found because each section of a tank has its own particular problems. Little relation was found between either chemical composition or porosity and resistance to glass attack. The importance of homogeneity of structure was stressed. Electro-cast blocks of mullite composition possessed the greatest resistance to corrosion. Various specimens were allowed to float in the glass during one melt, but all disentegrated except a sample of fused alumina and a block of very high alumina content.

After a furnace has been designed and constructed there follows the problem of analyzing the tank blocks and of interpreting the results.

An outline for a testing procedure, as suggested by Partridge[8] is as follows:

I. Test the quality of the block by:

A. Physical tests

a. Examination of texture

b. Examination of crystalline structure

c. Determination of density and porosity

d. Determination of firing treatment

B. Chemical Tests

a. Corrosion by acids

b. Corrosion by batch materials and dust

c. Corrosion by glass

II. The Examination of the quality of the glass as affected by the quality of the block.

Partridge likewise suggested that the testing of blocks by constructing small tanks was likely to furnish the most direct information of a practical nature.

Hyslop[9], at the 1936 International Glass Congress, made the recommendation that for better analysis and

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[8]Partridge, J.H., The Testing of Refractory Blocks, Jour. Soc. Glass Tech., 20, 548-51, (1936).

[9]Hyslop, J.F., Testing of Tank Blocks, Jour. Soc. Glass Tech., 20, 566-68, (1936).

classification of tank blocks, more emphasis should be placed on certain aspects of testing, such as, metamorphic tendencies or physical transformations, and on chemical composition of the refractory.

Rooksby and Partridge[10], give a brief but complete description of the technique used to examine glass tank blocks by use of X-ray analysis, by a method known as the powder method. There is no need in this paper to go into the discussion of the technique of the X-ray analysis. It is sufficient to mention X-ray investigations because of of its wide useage in tank block investigations. Kai-Ching Lu[11], Insley[12], and Naviss[13], and others have examined corroded blocks by X-ray analysis.

Microscopic analysis has also been widely used to investigate tank blocks, before installation in the test furnace, and after contact with molten glass.

This work is concerned primarily with the design and

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[10] Rooksby, H.P., & J.H. Partridge, The Examination of Glass Tank Refractories by X-rays, Jour. Soc. Glass Tech., 24, 109 ff, (1940).

[11] Kai-Ching Lu, Glass Tank Refractories..., Ohio State Exp. Stat., Bul. No. 44, (1928).

[12] Insley, H., Jour. Am. Cer. Soc., 9, 635-38, (1926).

[13] Naviss, N., Jour. Am. Cer. Soc., 8, 296-302, (1925).

construction of an electric glass tank, but to obtain any idea of the nature of the materials in the tank block, before and after contact with the molten glass, these other methods of testing should be employed in conjunction with the tank.

DESIGN OF FURNACE TANK

The following ideas were incorporated into the construction of the tank for this thesis. The superstructure is to be carried independently of the walls by an ironwork bracing. First, it is undesirable to have the blocks support the side wall and crown thrust. Secondly, it is desirable to be able to leave the side walls and the crown intact and undisturbed while placing or changing the actual tank blocks, as a good crown may last for years. The side wall is to be set outside the block line, as shown in the accompanying drawings.

Another matter to consider in the construction is that the life of a tank block can also be increased by protecting the tops from direct heat.[14] In order to protect the tops of the blocks from radiated heat or flame, the simplest thing to do is to build the side wall and

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[14] Haller, P., Cer. Ind. 32-33, 27, (Mar., 1939).

tank block in a flush vertical line. This prevents the tops of the blocks from getting hotter than other parts, and also prevents the corrosive batch dusts from being deposited. The objections to this type of design have been presented above.

The size of the furnace must be such that the expense involved will not be excessive, yet of such size that sufficient refractory area can be exposed at one time, and also, that in its operation the tank will enable currents to be set up in the molten bath.

The tank designed herein has inside demensions of 12 wide, 12 inches deep, allowing for a depth of glass of 10 inches, and length of 34 inches.

A bridge was incorporated in the design, allowing 10 inches of glass melt in the refining chamber.

The bottom of the tank should be of one solid piece of refractory, 12" x 6" x 46", to eliminate all joints, and to simplify construction. It will be shown later that the presence of joints increases the degree of attack and corrosion by the molten glass. The bottom block need not be composed of a test refractory material, unless, of course, a complete tank were desired to be constructed out of the test material. It is advisable to use a tried and tested refractory for most of the tank, with test pieces of smaller size, probably 9 inch brick, laid up at various sections of the walls. Brick must be placed at various parts of the tank, as the different sections are not subjected to the same corrosive action. In general, the bridge wall will recieve the most severe corrosive action.

It might be well to mention at this point that the blocks in the melting chamber are exposed to much more severe conditions than those in the refining chamber, with the end-wall in the melting chamber being corroded most.[15]

The usual glass melting furnace refractories are silica brick and clay blocks. The silica brick are used in the crowns and upper side walls where they are exposed to the action of dusts and gases in the furnace, but not to the direct solvent action of the molten glass. The clay refractories are generally used in the lower side-walls and bottoms where they contact the glass. The brick through which the Globar elements extend would best be of high heat duty brick.

The silica brick masonry requires a siliceous mortar. This could be obtained by mixing fine sand with diatomaceous earth, with about 1% slaked lime added as a bond.

The firebrick masonry requires a refractory aluminous mortar. This could be prepared by mixing a fine-grained

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[15]Pendergast, & Insley, _op_. _cit_., p. 460.

grog with a minimum amount of plastic clay tempered with water. Alumdum cement would also serve the purpose.

SPECIFICATIONS FOR TANK CONSTRUCTION

Section One. Tank Block Sizes.

The bottom block is to be one piece, of high grade fire-clay material, 24" x 6" x 46".

The melting compartment is to be of one end-wall block, 24" x 6" x 12", or its equvalent in 9-inch straights. The melting compartment consists of 2 side-wall blocks, 22" x 6" x 12".

The bridge wall is to be 12" x 4" x 12", with a square opening 4" x 4" at the bottom center.

The refining compartment consists of 1 end-wall block 24" x 6" x 12", and 2 side-wall blocks 12" x 12" x 6".

Section Two. Crown.

The span of the crown is 24", with a total rise of 5", there being $2\frac{1}{2}$" rise per foot of span. The arch is 9" in thickness, not considering insulation, and composed of silica brick.

No. 1 wedge brick, 9" x $4\frac{1}{2}$" x ($2\frac{1}{2}$" - $1\frac{7}{8}$") : 6 required per course, or a total of 36 brick required.

No. 2 wedge brick, 9" x $4\frac{1}{2}$"x($2\frac{1}{2}$" - $1\frac{1}{2}$") : 11 required per course, or a total of 66 brick required.

The skew block required is a 6" feather edge. A total of 16 are required. The brick size is 6" x $4\frac{1}{2}$" x ($2\frac{1}{2}$" - $\frac{1}{8}$").

Section Three. Side-wall Superstructure.

A minimum of 260 superduty firebrick are required for the support of the crown, standard 9 inch brick. The Globar elements will extend into the furnace through holes in these brick which transmit the crown load to the supporting iron sheet and pipe.

Section Four. Plate or sheet steel.

1. The load of the superstructure is transmitted to the iron pipe and hence to the floor going around the tank blocks. The superstructure rests on a $\frac{1}{4}$" sheet, which in turn rests on the supporting pipe.

Plate required, $\frac{1}{4}$" thick: 2 pieces, 42" x 9"
2 " , 46" x 9".

2. The tank blocks are kept in place by a steel cover welded to the supporting pipe . The bottom block rests on a $\frac{1}{4}$" sheet which in turn rests on the I-beams.

Plate required, $\frac{1}{4}$" thick: 2 pieces, 46" x 18"
2 " , 24" x 18"
1 piece , 46" x 24".

Section Five. Iron Pipe.

The superstructure is supported on iron pipe of 3" nominal diameter, with base plates. 18-17" lengths are specified.

Section Six. Other Steel Required.

1. I-beams. The tank blocks rest on I-beams, which serve to elevate the tank and allow for some degree of natural cooling of the blocks. 9-24" beams are needed; 7.7 lb. per ft., 4" x $2\frac{1}{2}$" size.

2. Standard Steel Channel Beams. The thrust of the crown is taken by channel buckstays, connected at the top and bottom by tie-rods. The channel specified is 50" long, 9 lb. per ft., 3" depth and $2\frac{1}{4}$" flange. A total of 300 ft. is required.

3. Tie-rods. These extend from the channel beams across the furnace. 6- $\frac{3}{4}$" rods are specified, with at least 12 nuts and washers. It is desirable to provide for the expansion of the silica brick in the crown. Thus expansion springs must be placed at the ends of the tirods. The length of each tierod should be at least 60".

Section Seven. Heating Elements.

Globar "AT" Type heating elements, a product of the Carborundum Company of Niagara Falls, New York, are used. A 1" diameter rod is required, with an overall length of 46". These rods have 2" of metallized contact at each end.

6 rods are specified. The effective heating area of each rod is 75.40 sq. in. Free air calibrating specifications are: 97 volts, 79 amperes, 1.228 watts. The

maximum surface loading (watt loading) is 110 watts per sq. in. The number of rods required must necessarily be found by actual tests and experimentation. However, 6 rods are in the furnace designed-4 in the melting compartment, and 2 in the refining end which is kept at a lower temperature. Suffieient room must be left at the melting end for introduction of the batch.

The maximum temperature at which these elements operate is 2,750F or 1510C.

The "AT" Type of element has the end that extends beyond the outside furnace wall, metalized with aluminum, over which a special aluminum braided terminal strap is placed and held in position with the use of a special type of clamp. The Globar elements require no artificial cooling at the ends.

Section Eight. Insulation.

The heat lost by conduction through a non-insulated furnace roof is very great, and can be minimized by proper insulation. When the roof is insulated the outside of the bricks becomes very hot and thus a small difference in thermal expansion is produced, which results in a better and more solid face to face contact between the brick. A silica brick roof in which the inside face of the brick is 2,500F. and the outside face is 1,700F. is a stronger and more monolithic structure than if the outside face were cooled to 500F. by direct contact with the atmosphere[16]. More uniform heating of a silica brick tends to increase the crystal homogeneity and reduce spalling.

The type of insulation is not specified. A 2¼" course of C-22 insulation brick, Johns-Manville Co., may be laid on top of the crown, or a course of K-20 brick, Babcock and Wilson, Co., may be used. Insulation is best applied after the furnace has been raised to operating temperature.

Section Nine. Cooling.

The artifucial cooling of tank furnaces by air and water is generally regarded as essential. According to Haller[17] the only cooling necessary with good tank design should be on the metal line at the melting side and on the top of the throat cover.

With no bonding agent used for setting the blocks, the blocks must usually be cooled in order to solidify the glass in the joints, to prevent leakage of the glass. If the joints should leak, especially at the start of the tank operation, clay should not be used to daub up the cracks. It is better to let the glass flow out and cool

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16 Pike, R.D. Insulation of Glass Furnace Roofs, Jour. Am. Cer. Soc., 12, 56, (1929).

17 Haller, P., Cer. Ind., 32-33, 28, (Mar., 1939).

to form a seal. No provision has been made in this design for cooling, other than that obtained by atmospheric currents. Portable fans could be used. The tank is set on I-beams to allow for air circuation beneath the bottom block.

The drawings for the design of the model tank are included in the following pages.

OPERATION OF TANK

The batch enters the furnace melting chamber at the top end, just under the arch. End brick can be removed to accomodate the batch. Periodic batch feeding procedure, much like that reported in the U.S. Bureau of Standards investigation previously referred to on page 9, could be patterned after.

Getting the batch over the tank block and keeping it off the Globar elements may present some problems. A refractory tube would serve as a satisfactory shute for the batch.

Raw batch should not be allowed on the refractory block walls[18]. The fluxes in the batch are present to dissolve the refractory sand in the batch, not the

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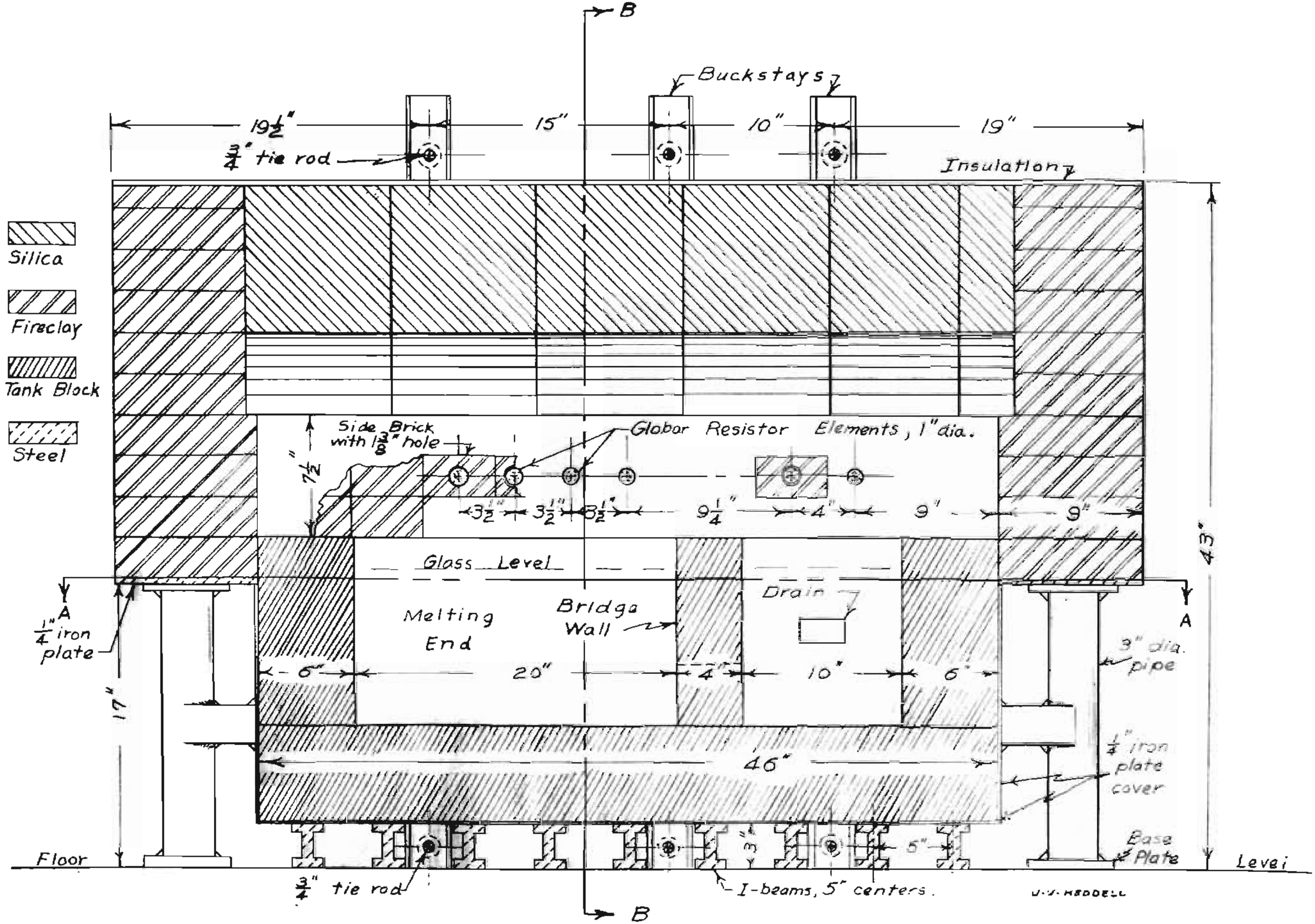
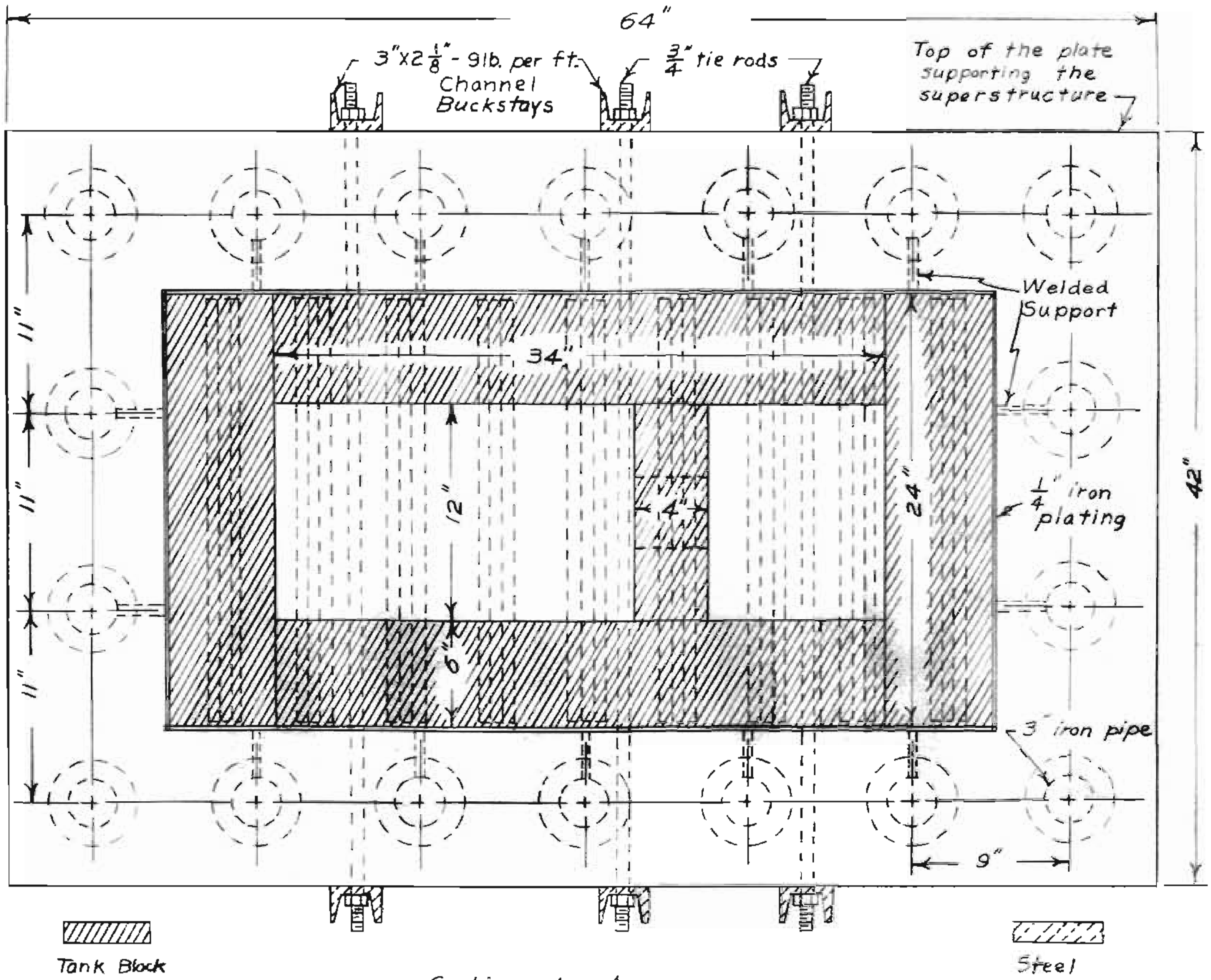
[18] Haller, P., *op. cit.*, p. 27.



Model Electric Glass Tank Scale: 1½" = 1'-0"

Figure 1.



Section A - A

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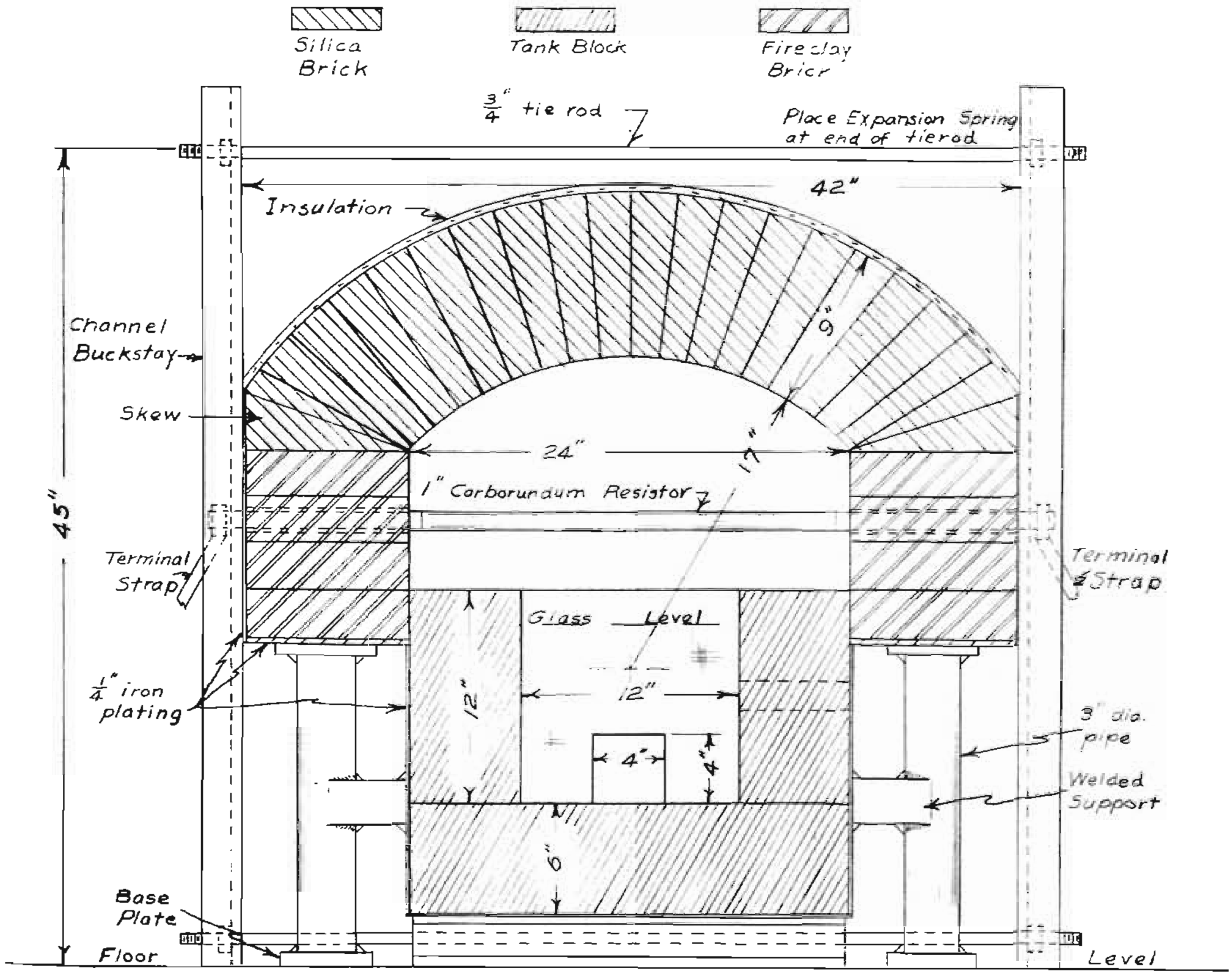
Model Electric Glass Tank Scale: $1\frac{1}{2}" = 1'-0"$

Figure 2.



Section B - B

J. V. HEDDELL

Model Electric Glass Tank Scale: $1\frac{1}{2}'' = 1'-0''$

refractory material in the tank block. Chemical attack on the block will be serious. It will produce cord which will spoil the glass product. There will be a great tendency toward the production of stones from the refractory. And lastly, the life of a block exposed to continuous attack by raw batch will be serious shortened.

According to the nature of the glass to be melted in the tank, the temperature will run from 1,200C to 1,440C.[19] The lower temperature is considerably higher than that given as the operating temperature of the U.S. BUREAU of STANDARDS tank [20]. The Globar heating elements chosen in the design herein have a maximum temperature range above that required to melt any composition of glass that might be introduced in the tank.

REVIEW OF LITERATURE

It is well known that molten glass attacks the walls of glass tanks and dissolves them, and it has often been assumed that this subject falls primarily or exclusively in the field of pysical chemistry and can be understood only in terms of phase equilibrium. It is true that an understanding of the phase equilibrium is a great aid to

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[19] Devillers, & Valerwyck, <u>op</u>. <u>cit</u>.

[20] Pendergast, & Insley, <u>op</u>. <u>cit</u>.

understanding and interpretang the solution processes.

According to Preston[21], if the walls were subjected only to chemical attack they would last almost indefinitely. As was shown by Preston, and others, erosion can generally be attributed to two factors, namely: (a) solution by chemical attack; (b) currents and movement of the glass that "wash" the refractory.

The method of corrosion of tank blocks has been the subject of a good deal of study and investigation. Very often an investigator will come to a certain conclusion and stress it so strongly that the implication is left that there is but one method by which the block dissolves. Actually, there are a great number of factors involved in the solution of blocks, no one of which greatly predominates over the others.

Enough tanks have been examined[22] to indicate that a very large percent of the corrosion of blocks is a result of the formation of fine cracks on the inside surface extending gradually into the block, often not reaching the outside surface, the block going into solution at the line where the crack starts, at the indide wall. The

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21 Preston, F.W., The Behavior-And Misbehavior-of Glass in Tanks, Am. Cer. Soc. Bul., 15, 411, (1936).

22 Flint, F.C., & A.R. Payne, Tank Block Corrosion by Shelving, Jour. Am. Cer. Soc., 9, 613ff, (1936).

block goes into solution quite rapidly along this narrow zone and solution is mostly upward from the crack, leaving a shelf at the bottom. Photographs of blocks from large commercial glass tanks show supporting evidence of this shelving effect. Flint and Payne point out that about one-third of the block in the refining chamber of a tank which was examined were in good shape after firing; the rest showed signs of cracking. There was also noted that were the temperature was about 2,350F. the glass attack was not so rapid as in the melting chamber with a temperature of 2,600F. Most of the blocks showed more corrosion near the top than at the bottom, although the cracks were almost evenly distributed throughout.[23] There may have been poor firing or drying of these block in manufacture to cause cracks, or heating up of the tank may have caused them. Such cracks may develop through spalling, too, especially during periodic batch feeding. It was noted that the cracks causing shelving were barely able to be seen. No cracks extended to the outside wall, and most a all of them were horizontal. Blocks broken did not break along these cracks. Glass penetration into the crack seemed to have been a sixty-fourth of an inch at most, but this small penetration was sufficient to cause more

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[23] Ibid, p. 622.

and faster corrosion than produced at a smooth face.

The upward penetration of the refractory block by the glass may be explained as follows.[24] The glass dissolves the exposed block surfaces and forms a clay-bearing glass. This clay-bearing glass is heavier, with a greater density, than normal glass, and thus sinks. Dissolving of the blocks proceds in proportion as the clay-bearing glass is removed. However, if this glass is not removed from a given portion of tank block surface, such glass, at and near the surface, becomes saturated with clay and further solution of the surface nearly stops. Considering the formation of a shelf, the shelf holds the more saturated, viscous glass longer, so it is not eroded as fast, whereas the roof of the crack is quickly exposed to fresh glass, which is farther away from equilibrium with the solid phase.

The clay-bearing glass forming at the tops of blocks tends to flow down over the vertical faces of the blocks and protect them. Wherever there are horizontal joints between the blocks, or defects in the surface of the blocks that glass can get into, downward-facing surfaces are present, from which the clay-bearing glass, being relat-

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24 Ross, D.W., Wearing Away of Tank Blocks, Jour. Am. Cer. Soc., 9, 645-49, (1926).

ively heavy, readily settles and flows away and very rapid solution of the blocks results. Such upward eating is characterized by circular holes approximately three-eights inch in diameter which are drilled vertically upward. If the blocks are not well bonded, pieces of it may become dislodged and float away, or it the face of the block shrinks much in use, cracks may open up in it.

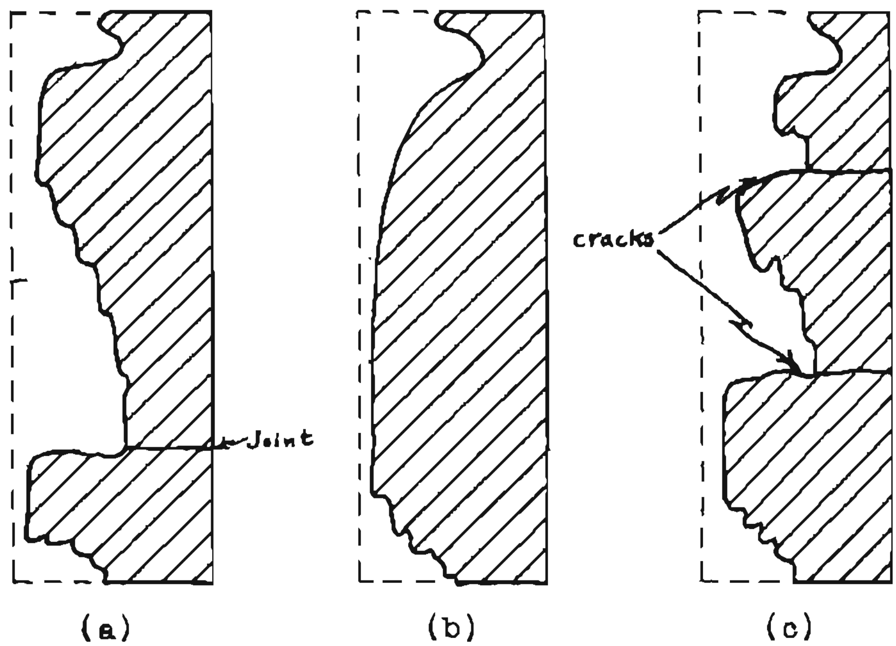

Figure 4.

Figures 4(a), 4(b), and 4(c) illustrate corrosion according to Ross[25]. Figure 4(a) is characteristic of a two-course

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25 Ibid.

sidewall. Figure 4 (b) is characteristic of a single course sidewall, or solid block, showing the advantage of eliminating as many joints as possible by the use of larger blocks. Figure 4 (c) shows the effect of upward eating of blocks due to cracks in the block. This appears on the tank wall as deep, hollowed pockets, more or less circular in shape.

According to Ross, whose work has been cited, the deeper the horizontal joints are below the surface of the glass, the less corrosion will occur. Thus less corrosion will occur at horizontal joints between the bottom and side walls than at horizontal joints in the side walls themselves.

Rosenhain[26] investigated the phenomena of refractory attack by measuring the decrease in diameter of cylindrical clay bars immersed in molten glass. Hyslop[27] carried out a similar experiment with respect to the density of the solute-rich glass and the size of particles of the refractories.

Sosman[28], in an investigation of the principles

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[26] Rosenhain, W., Jour. Soc. Glass Tech., 3, 93-116, (1919).

[27] Hyslop, J.F., & R. Gumm, & H. Briggs, Jour. Soc. Glass Tech., 10, 405-24, (1926).

[28] Sosman R.B., Jour. Am. Cer. Soc., 8, 191, (1925).

governing the corrosion of fireclay by glass, pointed out the importance of the speed of the surface reaction or the rate of reaction between solid clay and liquid glass at the surface, and the speed of diffusion. He pointed out that comparatively small increases in the glass tank temperature will greatly increase the rate of reaction between the tank block and the molten glass. The matrix of the block is of importance, since as long as the glass in the matrix or bond is of much greater viscosity than the glass in contact with the block face, actual solution or corrosion of the block will be slow. With modern types of dense, well-burned tank blocks, it appears that erosion by the moving glass is a less important factor in block wear than actual solution or corrosion.

Rees[29] made an investigation to compare the behavior of aluminous clays and sillimanite with fusion-cast mullite block in contact with molten glass at 1,350-1,400F. Tests were made on four fireclays, three sillimanite materials, and some fusion-cast material. Test pieces 3" long and 1" square were immersed in molten glass, the volume decrease after 12 hr. periods of testing being taken as a measure of the corrosion.

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[29]Rees, W.J., Glass Tank Refractories, Jour. Soc. Glass Tech., 23, 413, (1939).

Rees concluded from his investigation that:

1. Well-fired, dense, sillimanite blocks were more resistant to attack by glass than aluminous fireclay.

2. The presence of free alumina is an advantage in the sillimanite block.

3. A dense block structure produced by proper grading of materials in manufacture gave the best tank block.

4. Block pressed under 20,000 psi in manufacture gave results comparable with fusion-cast block of similar composition.

Rees indicated that the fusion-cast block were the most desirable because it was easier to make them dense and homogeneous by cast methods of formation. Fused-cast refractories generally contain not less than 80% alumina, the rest being chiefly silica.

The alumina and silica present in a tank block tend to form the mineral mullite-$3Al_2O_3 \cdot 2SiO_2$- when the block is fired to a sufficiently high temperature.[30]

Rees[31] reported from a study the following conclusions regarding block composition. That the Alumina-silica

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[30] Thompson, F.S., & H.I. Vormelker, Mullite Content of Some American Tank Blocks, Jour, Am. Cer. Soc., 9, 639, (1926).

[31] Rees, W.J., Alumina-Silica Minerals in Glass House Pots & Tank Blocks, Tran., Am. Cer. Soc., 38, 527, (1939).

mineral found in fireclays after firing is of the composition $3Al_2O_3 \cdot 2SiO_2$, and called mullite; and that the proportion of mullite present in fired clay increases with the alumina content of the clay and with the temperature and duration of the heat treatment.

The corrosion phenomenon may well be considered from the standpoint of chemistry. The ordinary glass is more or less saturated with silica, lime and soda, and deficient in alumina. It is shown in the system SiO_2-$Na_2O \cdot SiO_2$-$CaO \cdot SiO_2$ [32] that the commercial soda-lime glass has a composition very near to that of the eutectic, 73.5% SiO_2, 5.2% CaO. On the other hand, the refractory is saturated with respect to Al_2O_3 and SiO_2, and unsaturated with respect to Na_2O and CaO. Thus Alumina, and to a smaller extent tests show, silica, will be dissolved from the block into the glass. After a time the glass will be saturated with alumina in the zone next to the block face. This alumina combines with silica, and crystallizes out as a white, porcelain layer, principally mullite. This mullite layer has been reported also by Insley[33] who used microscopic methods to identify the needle-like crystals of

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[32] Morey, A., & J. Bowen, Jour. Soc. Glass Tech., 9, 245, (1925).

[33] Insley, H., Notes on Behavior of Refractories..., Jour. Am. Cer. Soc., 7, 585, (1924).

mullite imbedded in a matrix of glass. Insley also found that further within the refractory the crystals are small and poorly developed and amorphous materials still remain in the body. The glassy matrix of the white layer seems to dissolve readily in the molten soda-lime glass, and the surfaces of the mullite crystals also show traces of corrosion and solution.

Next to the contact zone but within the soda-lime glass there is very frequently a layer of small, hexagonal plates of corundum - Al_2O_3.[34] It appears that as the aluminum silicates dissolve in the molten glass the concentration of alumina in the contact zone increases until the solution is supersaturated with respect to alumina, and corundum is deposited on further solution of the clay. Since corundum crystallizes out at the glass-block surface of a mullite block, it indicates that corundum blocks would be chemically resistant to glass action. Experiments have shown that corundum and fused alumina blocks were resistant to corrosion chemically but that they lack mechanical resistance and were badly affected by currents in the glass. However, the problem of cord formation may be a serious one when aluminous fireclays

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[34] Insley, H., A Study of the Orgin and Cause of Stones In Glass, Jour. Am. Cer. Soc., 6, 715, (1923).

are used, and it would therefore seem desirable that the aluminous materials used should be those, such as, sillimanite, which are resistant to solution in glass. Sillimanite goes into solution slower and forms a thinner layer of alumina-rich material on the block face.[35]

Next to the zone of corundum and farther from the refractory is a zone of nephalite, $Na_2O.Al_2O_3.2SiO_2$, the crystals containing considerable glass inclusions. It is probable that the nephalite crystallizes during the cooling of the melt. The zone of corundum is not always found where the molten glass has contacted a refractory block. Where the flow of glass past the refractory wall is rapid the corundum is probably soon swept away or dissolved in the unsaturated solution, and if the clay refractories are high in silica the corundum may never form.[36]

The relative solubility of corundum as compared with the aluminum silicate and the silicates of alumina and the alkalias indicates that a high alumina refractory for the lower side-walls and bottom blocks of tanks melting soda-lime glasses would offer greater resistance than clay refractories.

Glass tanks are constructed with relatively large blocks to reduce the number of corrosion joints. However,

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[35] Rees, W.J., op. cit.

[36] Insley, H., op. cit., p. 720.

the point of severest attack is at the metal line, or flux line, as shown in Figure 4. It is important to reduce this flux line attack as much as possible by cooling or better still, by proper selection of the block. Various cooling devices have been employed to cool this line, such as refractory rollers and water jackets within the glass bath near the glass level. The life of the refractory is dependent on the rate and degree of cutting and erosion at the flux line.

The effect of glass ingredients has been studied to some extent. Sodium sulfate and some other sodium compounds appear to be much more active on flux blocks under strongly reducing conditions than under oxidizing conditions. The blocks appear to be destroyed by actual penetration of the sodium compounds into the pores of the block, rather than by solution at the surface. It appears that under such reducing conditions the composition of certain compounds is altered, possibly with the formation of some free Na_2O which is very active.

As is commonly known, sodium carbonate is not readily decomposed by heat alone at ordinary glass-melting temperatures. Some of the other sodium compounds used in glass manufacture liberate some free Na_2O, especially under reducing conditions, which is active on the blocks during the interval until it is converted to the carbonate by the furnace atmosphere.

Many manufacturers add salt cake to the batch. On rising to the surface the salt cake comes into contact with the reducing furnace atmosphere and dissolves any siliceous matter present at the surface of the glass, and thus prevents the formation of a siliceous scum. The absence of such scum allows heat to come into more direct contact with the melting glass batch. The percent of salt cake added may be in excess of that required to prevent scumming, and this excess attacks the blocks increasing the flux line corrosion.

It might be mentioned that if after a period of operation the flux line is badly eroded while the rest of the block is in good conditiom, the glass level could be lowered a few inches to produce a secondary metal line, and thus increase the tank life.

Clay refractories exposed to the gases and dusts in the furnace atmosphere are much more affected than silica refractories.[37]

CONCLUSIONS

The duration of a tank furnace run of operation,

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37 *Ibid.*

in so far as it is governed by the properties of the tank blocks, is determined first, by the durability of the block, that is, by the rate of solution, and secondly, by the effects produced by this solution in the glass.

One of the most important properties is uniform corrodibility. In manufacture of tank blocks, it is sometimes an advantage to use some siliceous material as grog instead of the usual fireclay grog, as siliceous particles which become detached from the block are more readily dissolved by glass than firelay is, and so do less harm. For this reason, it is preferable to use a slightly less resistant material if it will corrode more uniformly than a more refractory one which forms "seeds".

It is preferable to use silica in the crown brick, as it tends to expand rather than contract when heated, so there is less chance of their being dislodged; and also, any silica particles falling off into the melt does less harm than pieces of fireclay, as mentioned above.

Glass tank blocks may be preserved by cooling them externally. This cooling reduces the temperature of the blocks and prevents excessive corrosion, thus prolonging furnace life. This practice is wasteful of heat though. Insome cases, the cost of the loss of heat is less than that of replacing the blocks more frequently.

Furnace design should be considered as a factor in the life and solubility of the refractory block used as a lining.

Glass tank blocks are worn away largely by solution of downward-facing surfaces. Such eating is largely eliminated by horizontal joints. The deeper any joint is below the surface of the glass, the less it is eaten out. A method of placing the blocks to eliminate the vertical base-joint would be to extend the side-wall block to the bottom of the furnace, and not rest it on the bottom block; thus eliminating the type of upward eating known to occur at this point.

Electric heating of glass furnaces by radiation from carborundum resistors is possible and practical, with many advantages to be had over other forms of heating. Ease of testing and better control of heating can be had. The initial cost of the tank is also less than for gas or oil fired tanks. Globar resistors incorporated in the accompanying design are particularly desirable in that no external cooling of the elements is required.

The solvent power of the glass for the clay refractory is one great factor which influences the life of a refractory. A factor which quite often determines the life of a refractory is, not the rate of solution, but rather the penetration of the refractory by the glass.

The factors which influence refractory solution and penetrationare not the same. Aside from the penetration resulting from a local condition or defect, or a localized high temperature, the penetration of the refractory is determined by the character of the glass, and the pore space of the refractory. The property of the glass which primarily determines the degree of penetration is its fluidity and its viscosity-temperature relations, more than the solvent power of the glass for the refractory.

During the solution of the clay refractories exposed to the direct action of the molten glass corundum frequently crystallizes out because it is less soluble in the molten soda-lime glass than the aluminum silicates of the clays. High alumina refractories should be more resistant, therefore, to solution by the glass than fireclay refractories.

A well-fired aluminum silicate tank block contains well developed crystals of mullite, in contrast to the poorly developed crystals of mullite in an underfired block.

No furnace has, as yet, been constructed using the design given herein. It follows that no corrosion tests were performed by the writer. The conclusions given were based and obtained for the most part from related investigations which have been reported in the literature.

APPLICATIONS TO INDUSTRY

A knowledge, more inclusive and broader, of the comparative values of different types of refractories for glass melting furnaces would be of great value to the glass manufacturer, because the life of such furnaces depends mainly on the behavior of the refractories.

In selecting a tank block refractory, a manufacturer should consider the advantages and disadvantages of using an aluminous block or a siliceous one. The final choice by all manufacturers can never be the same because of the many factors which enter in the problem, each case requiring its own particular solution.

Longer tank life appears to be vavored by the production by tank block makers of blocks having a minimum of shrinkage after being placed in the tank, and containing a minimum of mechanical defects that the glass can penetrate.

The user of tank blocks can obtain longer tank life by the elimination of horizontal joints between the blocks.

Constant careon the part of the glass manufacturer during heating up of the tank is important, for cracks formed in the blocks during heating will allow for increased corrosion of the blocks and decreased tank life.

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