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LEAD CHEMICAL CONSTRUCTION BULLETIN NO. 23

SUBJECT: APPLICATIONS OF LEAD-ACID BRICK SYSTEMS IN CHEMICAL PLANTS

Attached is a reprinted article "Applications of Lead-Acid Brick Systems in Chemical Plants," an extraction of "Lead-Acid Brick Construction," by E. J. Mullarkey, Technical Director of L.I.A., presented at the 1958 meeting of the National Association of Corrosion Engineers in San Francisco, which appears in the February, 1959 issue of "Corrosion."

It relates latest practices and experiences, and refers to a suggested new test method for locating in-service leaks with the aid of radioisotopes.

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Robert L. Ziegfeld

Secretary

Applications

of

LEAD-ACID BRICK SYSTEMS

in

CHEMICAL PLANTS

by

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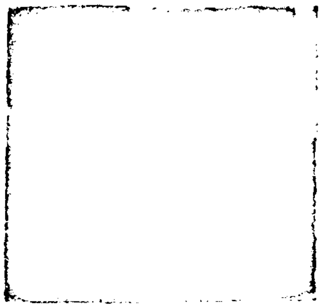

Figure 1—Effects of pitting and scabbing on lead. The two top pieces show the pitting resulting from combinations of sulfuric acid and organic compounds. The bottom piece shows the absence of these effects when supplementary acid-brick lining is used.

Applications of Lead-Acid Brick Systems* in Chemical Plants

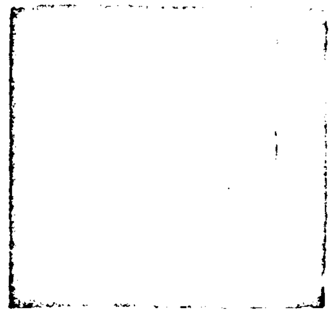

Figure 2—Vacuum concentrator body section lined with half-inch lead sheets.

Abstract

The use of lead-acid brick systems is reviewed for use with corrosive, abrasive and hot chemicals. This type of construction has good abrasion and erosion resistance, good thermal insulation, low cost, good general corrosion resistance and the ability to withstand high temperatures.

Suggestions are made regarding the techniques for installing lead-acid brick systems [illegible]. Case histories are given in which lead and brick is used to [illegible].

Some of the considerations involved in the use of [illegible] brick in lead-acid brick construction are discussed briefly. [illegible]

WHEN SELECTED as the most suitable membrane to resist corrosion, lead can derive some additional benefit from acid brick. Where combinations of sulfuric acid and organic chemicals are encountered, drilling or scabbing may occur when lead is exposed to their direct action (Figure 1, pieces shown at top). This is comparable to incipient, destructive pitting. When supplemented by brick (for other purposes perhaps), lead does not pit in this manner.

This is illustrated by a process vessel in which 35 percent sulfuric acid plus coal tars were held at 120 F. Originally the steel vessel was lined with 16-lb lead on the walls and 20-lb lead on the floor protected by a 4½-inch course of hard-burned, high silica, acid-resisting brick laid in and backed with acid-proof cement. The lead on the walls was not protected because it was thought the lower temperatures would not cause trouble due to creep. During the life of this structure (over 13 years) the lead on the walls was renewed three times; no repair was made on the lead on the bottom. Repairs and replacement of lead on the side walls during this period were necessary because of the scabbing and drilling action of the sulfuric-organic chemical combinations as shown in Figure 1. At the end of the 13-year period when the tank was torn down, the original 20-lb lead on the bottom was found to be in perfect condition. It was proved in this instance that lead alone was not suitable for this type of service but that lead with brickwork would give an almost indefinite life. The replacement tank was completely brick and lead lined. In other typical cases so-called termite type holes have been attributed erroneously to dirty lead.

In all, the common divider between harmful and harmless organic materials or impurities seems to be their polar versus nonpolar characteristics. Polar organics are electrically active and have absorptive tendencies thus influencing molecular size and therefore diffusion. As a result, polar substances have limited or more restricted penetrability than nonpolar substances due to the tendency toward large molecular size. Correspondingly, nonpolar materials such as gasoline, benzene and toluene penetrate acid brick rapidly but fortunately are not corrosive to lead. The reverse of the above is true in the case of plastics or elastomeric liners. There is little doubt that these observations indicate that lead should be protected by brickwork where scabbing or drilling occurs.

Prime examples of successful service are three Simonson-Mantius vacuum concentrators operating in series on spent acid being reclaimed at National Petro-Chemicals Corporation refinery at Tuscola, Ill. A body section from one of these concentrators is shown in Figure 2. These units, over ten years old, have been operating continuously on 80 to 92 percent sulfuric acid used for the treatment of petroleum distillates and for the manufacture of alcohols. The acid to be reclaimed contains hydrocarbon impurities.

Savings in Cost Cited

Considering metal construction costs using membrane materials, the cost of supplementary construction being essentially the same for all membranes,[1] lead gives what amounts to a floating investment. After the useful life of the original lead lining has expired, the scrap value of more than half the original cost is recoverable. Table 1 gives data on the costs relative to several types of installations.

If the scrap value of lead is not considered, the comparative cost as given in Table 2 is not important in selecting a membrane. With lead and its first replacement considered, the comparisons are substantially altered. These figures are based on a nominal lead scrap price of ten cents per pound, corresponding roughly to 2/3 the market value of pig lead. Thus it is seen lead's scrap value, plus lengthy depreciation schedules realized from long operation periods, justifies the use of lead.

Rules for New Construction

Experience suggests certain rules in addition to those relative to tank design.

1. Supports suitable to permit air circulation beneath vessels. Often acid brick lead lined steel vessels are used at high temperatures with the vessels placed on a flat bottom or rim in such a way that heat is accumulated at the bottom, thus placing brickwork in heavy tension and resulting in bottom failures.

2. Bottom should be dished where pressure is involved.

3. The inside surface of the steel tank should be cleaned either by shot or sandblast to assure complete freedom from scale or other matter. If sand is used, the surface should be washed down

TABLE 1—Comparative Cost Figures for Several Membranes.[(1)]

Membrane Linings	Thickness Inches	Installed Costs $ Ft²	Modified Costs $ Ft²
Natural Rubber	3/16 1/8	[illegible] [illegible]	[illegible] [illegible]
Neoprene	3/16 1/8	[illegible] [illegible]	[illegible] [illegible]
Plasticized Polyvinyl Chloride	3/16	[illegible]	[illegible]
Lead Sheet	1/4 3/16	[illegible] [illegible]	[illegible] [illegible]
Hot Melt [illegible]	1/4	[illegible]	[illegible]

(1) Taking [illegible] lead scrap value [illegible] per pound.

(2) [illegible] Corrosion Research Corporation [illegible] and Allied Materials, March, 1948.

* Excerpted from a paper entitled "Lead Acid Brick Construction" by R. J. [illegible], Lead Industries Association, New York City, presented at a meeting of the 12th Annual Conference, National Association of Corrosion Engineers, San Francisco, March 11-15, 1956.

with water to remove residual sand.

All welds should be ground smooth; all sharp edges and corners should be rounded to a radius of not less than ½ inch. The surface then should be given one coat of red lead primer to retard rusting. A layer of ⅛-inch asbestos paper should be applied over the primer with silicate wels for optimum results. This acts as a cushion between the lead and steel to reduce abrasion caused by movement of the lead. Chemical grade 8- to 10-lb sheet lead usually is adequate and is generally used.

In the case of concrete vessels and floors requiring a lead acid brick lining, lead based paint also is used. New concrete structures should be coated with bitumen mastics prior to installing lead to prevent corrosion by free lime, the conversion of which to the harmless carbonate is time dependent.

4. The lead should be lapped over the top of the vessel to prevent seepage between the lining and the steel. Lower sheet lead sides should be lapped over the bottom sheet beyond the thickness of the first course of brick side wall and burned together. If trouble develops in this seam, the brick side wall would not have to be disturbed. This lap should be at least six inches.

In large vessels, however, or at high operating temperatures, it may be advisable to strap the lead to the outer shells. In many cases brickwork moves independently of the lead sheathed vessel and causes stress concentration at the strap joints. These points are trouble spots so two or three layers of asbestos paper to provide a cushioning and movement joint between brickwork and lead are recommended where support considerations warrant. Brickwork should be cut around the straps to allow for the thickness of the strap in lieu of asbestos paper.

5. After the lead has been properly installed and tested, it is lined with one or two courses of brick chosen for one or more of these characteristics: degree of acid resistance, minimum allowable porosity and degree of resistance to thermal gradient or shock.

6. Furthermore, steps should be taken to avoid contact with sodium ions in acid proof cements. This is done by bonding asbestos paper to the lead with potassium silicate solution before the brickwork is installed. Also a sheet of asbestos is used when furan resin cements are applied because they contain an acid catalyst. Although an asbestos membrane is not needed with resin and sulfur based cements, nevertheless two or three layers of asbestos paper are recommended to cushion movements between the lead, brickwork and resin-based cement.

Some, however, do not recommend the use of asbestos paper between the lead and the brick. Seepage through the brick wall saturates and loses it down, leaving pockets in which the liquid settles and concentrates, thus contributing to corrosive attack.

To prevent this, the following procedures are satisfactory. The lead is given a thin coat of resin cement or a plaster coat of silicate cement about ⅛ inch thick. This is applied the evening before the brick is to be laid and to no area greater than can be covered with brick the next day. The coatings have a tendency to crack if exposed too long. If another membrane is required besides the resin or silicate cements, glass

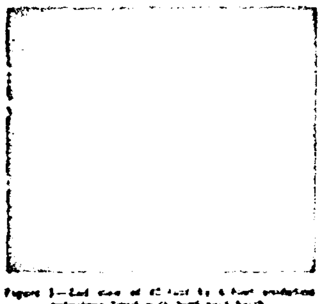

Figure 3—End view of 40 foot by 6 foot oxidation autoclave lined with lead acid brick.

cloth is used. Glass cloth is never applied alone. The brick is then laid up with the back of the brick dry. When there is no cement behind the brick, movement of the lining is made possible.

7. A sufficient thickness of brickwork is installed so that temperatures at the membrane surface will be reduced to 165 F. This measure helps to enhance mechanical and corrosion properties.

In the case of lead bonded to steel without tinning, creep or crawl will not occur up to 450 F; with tinning, up to 265 F is tolerated. But, it is essential that corrosion rates be carefully considered at temperatures affected by this method and particularly where tin has been used in the bonding process. Tin's use in bonding is largely a matter of commercial convenience and not a technical necessity. Bonding without the aid of tin can be accomplished. Also there is a deleterious effect of tin on the welds of backing steel joints in vessels constructed of lead coated or bonded steel sections, which affects the strength of the joint. Steel will alloy with tin causing porosity, the result of tin vaporization during the welding operation. However, lead-tin bonded steel (sectional) construction should stand up where little or no vacuum or pressure is involved, i.e., up to 265 F. Without tin, operation under vacuum or pressure to 450 F is permissible.

8. An attempt is made to obtain a thickness sufficient to reduce mean temperatures so that as temperatures increase the brickwork will be elongated more than the steel shell. The resultant differential expansion holds the lead in compression, thus assuring more than adequate support.

Replacement Case Histories

Equally important is repair type construction where lead is used as a stop-gap when other materials or techniques have failed to control corrosion. Lead often affords the fastest, most economical answer in problems involving process solutions or fume exhausts.

The 40 foot by 6 foot diameter oxidation autoclave at Calera Mining Company's Garfield, Utah, cobalt refinery is an example. This autoclave is shown in Figure 3. Originally of carbon steel construction, internally clad with a 10 percent Type 316 stainless steel, the autoclave was lined with one course acid brick and other supplementary materials (Epoxy paint, followed by glass cloth and asbestos paper applied with sodium silicate). Designed to operate at temperatures in the range of 400 to 450 F, the vessel was almost a total loss two years ago as a result of corrosion of the stainless steel and a complete deterioration of the supplementary materials. Interrupting a critical part of the oxidation process, the autoclave proved unsuccessful in containing the process slurry which is analyzed in Table 2.

TABLE 2—Analysis of the Process Slurry in an Oxidation Autoclave.

Material	Grams/Liter
Cobalt	60-75
Nickel	9.3
Iron (ferrous)	8.7
Iron (total)	10-11
Copper	3.4
Arsenic	3.6
H_2SO_4 (free)	100-200

In repairing this autoclave after considering other membrane materials and corrosion characteristics, it was decided to use a 12-lb sheet lead lining (with glass cloth and asbestos paper applied with sodium silicate) and one course of acid brick. During installation (burning of all seams and connections to lead nozzle liners), overhead lead sections were supported by a ¾-inch plywood template, a segment of a cylinder about six feet long supported by cables passing through the nozzle openings. The template was removed after the brick lining had been installed a course or so above the autoclave horizontal center line. After two years the lead liner is in excellent condition, and a relining job is not anticipated for at least five years.

Control of Exhaust Fumes

In the second case, in the new Bessemer City, N. C., plant of the Lithium Corporation, lead acid brick construction was selected after previous trials with combinations of stainless steel and plastic to prevent corrosion associated with exhaust fumes from a rotary kiln in which an ore and sulfuric acid mixture was roasted at temperatures in the vicinity of 500 F (Figure 4). The original plant design included a mild steel shell fog type scrubbing tower lined with a plastic coating. Duct work between the kiln and tower and from the tower to the exhaust fan as well as the exhaust stack were constructed of stainless steel. A short section of the duct ahead of the tower was fitted with nozzles to precool the gases in order to protect the plastic lining of the tower. However, in operation, small quantities of abrasive dust in the gases eroded away both the protective oxide film on the stainless steel ducts and the plastic lining of the tower. Consequently, the ducts, tower, fan and stack corroded.

The tower situation was corrected by lining the fan and stack with Neoprene. Neoprene could not be used in the duct work ahead of the tower because the temperatures there reached 500 F. A precooler was needed to protect the Neoprene lining of the tower. To protect the ducts and the tower, engineers designed a simple tower approximately 4 feet in diameter and 10 feet high of mild steel to act as a vertical duct to carry the gases to the bottom of the scrubber. This tower or precooler was

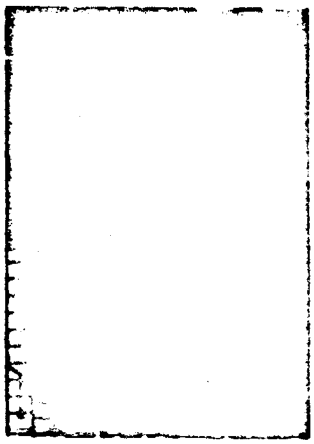

Figure 4—Rotary kiln. The [illegible] gases at 300 F enter the lead-and brick lined chamber at the left where they are cooled before entering the scrubbing tower at right.

lined with 1/4-inch sheet lead for resistance to corrosion, and one course of acid-proof brick was set to protect the lead against abrasion and to insulate against extremes of temperature. A 2-inch Teflon pipe fitted with Teflon nozzles was inserted into this pre-cooler from the top to supply the cooling water spray. A square horizontal duct of steel, lead and brick, similar in arrangement to the pre-cooler, connected the kiln exhaust hood to the pre-cooler. Because dust was expected to accumulate in the horizontal duct, brick was used only on the bottom and sides, leaving the top side accessible for cleaning. A mild steel plate protected on the underside with lead acted as a removable cover for the duct.

This installation was successful. The only maintenance to the duct and pre-cooler—in over two years of operation has been one replacement of the lead on the duct cover. The original installation of stainless steel and plastic required almost constant maintenance.

Like all methods of construction, lead-brick systems have certain drawbacks which may not seem important immediately. Locating leaks is a serious problem when they occur in process vessels in service where brick hinders quick location and repair, even assuming faultless lead construction and no damage to the lead membrane during the bricking-in process.

Methods of Locating Leaks

When a leak develops in bonded lead lined vessels, the chemical penetrates the steel shell at that point and is immediately detected visually. Subsequent repairs are made from the shell side without disturbing the brick lining. As a result, a bonded lead lining may be preferable to a lead membrane. There is no need to convince anyone of the difficulty in locating leaks by the weep hole method, which in most cases establishes the presence of a leak but little else. To find leaks, it is invariably necessary to tear up brickwork. This is tedious, time-consuming, costly in terms of labor and material and prohibitive in terms of down time. Radiography[4] offers a solution but is somewhat hazardous, doubtful and is costly in application and down time.

A more positive and economical method involves the application of radioactive tracers[5]. A low-level tracer-solvent method depends upon the amplifying effect a lead membrane has on a radiation-induced signal from a radioactive fluid source pumped behind and leaking through breaks in the lining. Scintillation or Geiger counters may be used as shown in Figure 5 to monitor the inside surfaces of a vessel to detect intensification indicative of a leak. Though simplified, Figure 5 describes the ease and accuracy of locating a leak within an area of no more than a few inches because of the build-up of radioactive material around the leak and to the change in attenuation of gamma rays attendant with the leak.

This approach is perhaps the simplest from the operational and cost standpoints but is not restrictive. The basic procedure can be used in reverse fashion—with the vessel filled and the outside surfaces monitored. But certain drawbacks anticipated in using this method were confirmed by the recent work of Sullivan and Coleman[6] reported at the 1957 Nuclear Congress. Working with lead lined wooden tanks, they found that the summation of radioactivity from all elements of volume within the tank was so much greater than that emanating from the leak channel itself that an activity differential could not be detected. In addition, if the optimum specific activity of 1.4×10^{4} mc/ml (NaI) had been used, a total activity of 560 mc @ ($0.50 per mc) would have been required. This was considered an impractical amount from both cost and health hazard standpoints.

A flotation technique based on the solubility of iodine in organic liquids was used to avoid these difficulties. This technique consisted of floating a thin water-immiscible organic layer containing radioiodine on the surface of water within the tank. When the liquid was raised and lowered past the leak site, a portion of the radioactive organic layer passed into the leak channel. Activity from this portion then could be detected easily when the organic layer subsequently was removed.

However, if the foregoing method were applied to brick lined tanks, the brick would act as a diffusing barrier to the organic layer. Moreover, because brickwork is inherently porous and capable of retaining quantities of tracer material, this may or may not be an obstacle depending on half life and the chemical activity of the isotope with respect to corrosion and process effluents. The behind-the-lead lining method should minimize if not obviate these problems if accomplished quickly. It is expected that only those bricks immediately adjacent to the leak would be affected and probably would be removed during cleaning and repair. In all cases detergent cleansing or chelation could be used advantageously to remove vestiges of the tracer.

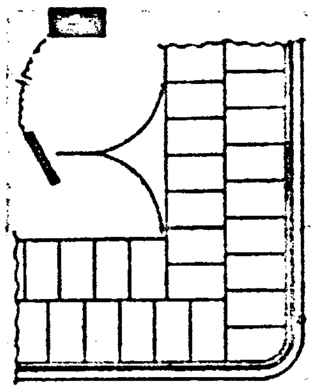

Figure 5—Detection of breaks by radioactive tracers. Geiger counter indicates concentration of radioactivity at the leak site.

Tracer techniques may be workable in the areas of homogeneous lead linings, sheet lead, or cage construction with or without brick supplements to determine the extent of corrosion occurring or, in another sense, forewarn of imminent failure. These would require studies of calibration and compatability with process effluents to prevent stoppages.

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