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LEAD INDUSTRIES ASSOCIATION

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ACID ALUM REACTION TANKS

Supplement to Chemical Bulletins Nos. 6 & 21 (Sent to Members on Dec. 16, 1946 and July 19, 1948, Respectively)

The bead catalytic cracking catalyst manufacturing process used by the Socony Mobil Oil Co., Inc. at Paulsboro, N. J. affords the conditions of service which constitute a major test of lead's ability in containing chemical corrosives. In particular the acid-alum reaction tanks have resisted to date the efforts made to successfully mitigate the corrosive conditions encountered therein for the past 13 years. This is not to imply that lead has failed this test but an attempt will be made to indicate the chronology of recorded events which led alternately to the use of loose lead linings, brick-plastic membrane linings, brick-lead membrane linings and finally to date a Haveg composition lining, and the circumstances surrounding the alternate use and disuse of lead. This bulletin summarizes and supplements Nos. 6 and 21, heretofore covering this installation.

Although lead is not in use at present in the alum reactor, the applicability of lead has been amply evidenced. It is only a case where the expeditious use of a material had been prevented by a lack of test methods or design developments applicable to mitigating expected failures encountered some 4 years ago. In this case history, there is excellent material on the sequence of events and steps taken in improving the serviceability of lead by proper design in the alum reactor, as well as information on the various other uses for lead in this area.

INTRODUCTORY HISTORY

In 1944, a total of 125 tons of lead was installed to handle the corrosive alum solutions in the Bead Catalyst Plant at Paulsboro where nearly two billion beads or 50 tons of finished catalyst per day are produced. The synthetic bead catalyst is used in the TCC process which at the time had recently come into extensive use in the production of high-octane gasoline. The beads are produced in lead lined forming towers from gel forming solutions consisting of sodium silicate and acid-alum (aluminum sulphate). Alum is produced in a boiling tank from aluminum trihydrate reacted with sulphuric acid.

PROCESS

Demineralized water is first introduced to the alum reactor whereupon sulphuric acid (66°Be) is added until the solution is 50 percent acid, filling the tank to a depth of 18 in. The temperature resulting from the exothermic reaction is further increased by the addition of aluminum trihydrate (purified

alumina) to 240° to 260° F. Additional alumina is added to maintain this temperature, and the reaction is continued for 1½ to 2 hours while continually agitated with steam which keeps the aluminum sulphate above its solidifying temperature of 210° F. After the reaction is completed, the batch is then diluted to make 23 percent aluminum sulphate which is kept for 4 hours at 130° to 140° F. Further dilution produces a 20 percent alum solution which fills the tank to 9/10 full and is liquid at room temperatures. The solution is then pumped out of the tank into a lead-lined solution preparation tank where it is further diluted to 10 percent. The average service of the reactor is one batch per day. It is readily seen that the combined effects of differential or cyclic heating, constant agitation, and abrasion and temperature level contribute to what is one of lead's severest tests.

EQUIPMENT AND PERFORMANCE

The reaction tank is 17 ft., 7 in. on the ID and 7 ft., 3 in. in depth, and was lined with lead initially after previous trials with a plastic lining in November of 1944 with 16-lb. chemical lead supported by vertical straps 4 ft. apart. This proved unsatisfactory after only 5 months operation and was consequently ripped out. Severe physical distortion of the lead had occurred and subsequent penetration of the alum solution resulted in replacement of the steel bottom and sides to a height of 18 in.

Since corrective steps were obvious and were dictated by the physical limitations of lead and not its specific resistance to the corrosive, a new tank lining was installed in March 1945 and put into service in June of 1945. Its bottom and sides were lined with 22-lb. tellurium chemical lead, and the slightly convex top, with 12-lb. chemical lead. The additional straps consisting of half-oval steel covered by 16-lb. tellurium chemical lead 7 in. wide were installed to give support every 24 in. on the side wall in contrast with the original 48-in. spacing. The bottom was secured by parallel straps sheathed with 16-lb. tellurium-chemical lead 16 to 18 in. apart and 5 in. wide bolted through the steel tank to supporting steel "I" beams beneath.

No repairs of this lining were required until October of the following year, 16 months later, when sporadic patching became increasingly frequent. All repairs were made with chemical lead rods. The walls showed the least amount of bulging or sagging between the straps and required the least repairs. Corrosion was least in the lower third of the vessel wall but above that, the wall area was exposed to hot corrosive fume in the presence of air, and some corrosion had taken place along the crests of the bulged lining. On the bottom, cracks and perforations had caused considerable trouble. Lead between the strapping had bulged in some cases as high as 3 in. above the tank bottom.

Trouble with the lining was severe because the product formed is liquid aluminum sulphate which seeps through occurring hair cracks into the cavity under a lead bulge, filling it, and later solidifying when the reaction ceases. Flattening of the bulges is prevented therefore and the bulge has to be cut open, and the solidified aluminum sulphate removed. Leaks were detected by weep holes; the presence of aluminum sulphate being noted by the appearance of stalactites.

This difficulty at the bottom was due primarily to the appearance of fine cracks adjacent to the welded seams, on the seams, on or adjacent to welds from earlier repairs, or along crests of the bulges. An article which appeared in "Corrosion Prevention & Control," December 1955, attests to the predominance of this type of failure.

(It is interesting to note that the area surrounding the nozzle of the aductor jet was free of failures. The lead was unaffected by the steam jet and the scouring action of the reacting solution.)

An attempt was made to correct the situation by using a brick lining to provide uniform support of the lining and also to insulate against the extremes of temperature and fluctuations thereof. However the cementing compounds used did not withstand attack by the solution and eventually the bricks loosened and proceeded to swirl around causing damage to the lead lining (or membrane) and to the agitating equipment as well.

In 19[illegible] the lead lining was removed and replaced with a 4½-in. brick and Basilon membrane lining which served only 2 years with frequent patching whereupon one of three reactors was relined with a brick-lead membrane lining which was installed using a suitable cement. This trial installation after a few initial leakages remained in service practically trouble-free until 1954 giving approximately 5 years' service. In fact, failures after 5 years of this type of service were expected and designed for. The only real difficulty presented at the time was not due to the repairs necessitated but rather in the difficulty encountered in finding the leaks. The weep holes were to no avail and the brick lining prevented the exact location of the leaks. Attempts made in repairing the lining resulted in a great wastage of man hours and extensive unnecessary tearing up of different parts of the lining. In short, test methods at the time were insufficient to cope with the problem of locating a leak under a brick lining, and resulted in the discontinuance in use of a serviceable brick-lead membrane lining.

In contrast to the situation 4 or 5 years ago, sufficient information now has been reported in the literature which precludes the possibility of removing a serviceable brick-lead lining for want of sufficiently adequate test methods or techniques for determining the location of flaws or leaks. The radiographic inspection procedures as recommended by Skill and Bracken ("Radiographic Inspection of Lead Linings," Paper No. 55-IA7-15, ASME Conf., New Orleans, Sept. 25-26, 1955, and as covered in Chemical Bulletins Nos. 63 and 67, sent on April 3, 1956 and Dec. 26, 1956 respectively) are suitable. When properly utilized all but a minimum of tearing up of brickwork to make repairs is preventable.

Further improvement in the techniques for determining leaks in acid brick-lead linings may be had possibly in the use of low level radioactive tracer-solvent methods which would be dependent upon the amplifying effect that the lead membrane would have on a radiation-induced signal from a radioactive fluid source pumped behind and leaking through breaks in the lining. Scintillation counters could be used to monitor the inside surfaces of a vessel in order to detect any intensification that would be indicative of a leak. After or before effecting repairs in this manner, detergent cleansing or chelation could be employed to remove vestiges of the tracer used where it presents a problem. The advantages of such a technique are indeed provocative.

Actually the installation although satisfactory was still capable of being improved. Similar installations by the Pennsylvania Salt Co. gave up to 15 years' trouble-free service under similar conditions of service. Understandibly, production requirements did not permit a more extensive deliberation of the problem. The long-term solution still seems to be in terms of lead but the present Haveg installation has not been sufficiently tested to demonstrate its adequacy in this service. But, it may well be noted that Haveg in over 50 percent sulphuric acid is not considered good usage. In fact a recent inspection revealed that frequent leakages are now occurring after their appearance initially a year ago after only 2 years' service.

To sum up the situation at the Bead Catalyst Plant, the bead forming towers lined with 3/16-in. chemical lead supported by a single steel strap at the top is still unaffected by corrosion from the dilute acid and aluminum sulphate solution, 5 percent H_2SO_4, 5 percent $Al_2(SO_4)_3$, 90 percent demineralized water at room temperature, after 13 years' uneventful service.

Lead lined storage tanks containing acid alum solutions diluted to 20 percent strength, and solutions further diluted for introduction to the bead forming towers, are still giving good service to date after 13 years.

A large proportion of the piping in this installation is lead which has been extended beyond the design stress levels without eventful failure and is still in good shape attesting to the durability of lead in this application. Lead pipe, valves and fittings in pump connections and lead return bends of sluice pipes under forming towers are all showing excellent usage.

An added point of interest is somewhat apart from the corrosion resistance of lead but still worthy of mention. In one of the storage tanks holding a solution containing 3 percent H_2SO_4, 4 percent aluminum sulphate and water, the lead adductor is held in place and supported by stainless steel bolts and clamps. In May 1956 after one year's service the bolts were corroded badly and the clamps were found on the bottom of the tank. This seemed incongruous since an Inco 60-day test revealed the following corrosion rates under these conditions:

for 304 type stainless	- .0007	in./yr.
316 " "	- .0003	"
Carpenter 20	- .00006	"
Ampco-8	- .0210	"
Lead	- .0005	"

The above results would hardly anticipate the precipitous failure of the stainless steel bolts.

Galvanically, the anodic behavior of stainless with lead was still unexpected but seems to answer for the failure. It has been known that in the absence of air, or oxygen, acid solutions can cause a reversal of lead-stainless positions in the emf series such that stainless becomes anodic, but the temperatures encountered, 120 to 130° F., and the presence of air precluded this possibility. It is another anomalous occurrence which cannot be explained readily. The bolts were subsequently changed and insulated with no further occurrence to date attesting to the galvanic nature of the problem.

SUMMARY

In this case history it is indicated that lead-acid brick linings can be used probably more effectively than anything else in acid-alum reaction tanks and under similar conditions by the use of improved methods now at our command. This type of construction has been handicapped, not by corrosion or mechanical failure, but by the difficulty of locating leaks and making repairs. In locating such leaks radiography has offered a solution. Another solution, possibly more economical and positive, is suggested through the use of radio-active tracers. Although this method has not been tried or proven in practice, the Association is anxious to cooperate with anyone having this problem in the hope of finding the most convenient and economical method of detection.