Damage Assessment of Concrete Sulfur Storage Structure in Petrochemical Industry

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ABSTRACT: In petrochemical industry, gas sweetening process results in the formation of acid gas consisting of H_2S, CO_2 and water vapor, which is sent to the Sulfur Recovery Units to recover sulfur. Molten sulfur maintained in a liquid phase at temperatures ranging from 130 °C to 160 °C are stored in reinforced concrete sulfur pits, constructed below grade to facilitate gravity flow. The reinforced concrete structural elements in sulfur pits are exposed to acidic gases and sulfuric acid vapor fumes at high temperature resulting in delamination, spalling, cracking and reinforcement corrosion instituting threat to structural integrity. This paper presents the field and laboratory investigations conducted on a 30-year-old, in service sulfur pit. NDT based investigations of the top slab of the pit was carried out using the ground penetrating radar, ultrasonic pulse echo, and half-cell potential measurements. Effect of high temperature molten sulfur exposure on concrete in sulfur pit is examined using petrographic examination, SEM/EDS and XRD tests.

1 INTRODUCTION

Natural gas obtained from Saudi Arabian sour gas fields contains significant amount of sulfur in the form of hydrogen sulfide. As a part of the gas treatment process, it is sent to the sulfur recovery units (SRU) to recover Sulfur. Typical SRU consist of a thermal reaction furnace, waste heat boilers, and a series of catalytic reactors (converters) and condensers. The sulfur generated from the process is stored in below-grade reinforced concrete sulfur storage tank (sulfur pits). (GPSA 2004). The sulfur pits reinforced concrete structures are subjected to aggressive environment involving exposure to sulfur, sulfuric acid, acidic vapor and moisture and elevated operating temperature between 285 ºF to 315 ºF (Kline 2004, 2006). Deterioration of the roof slab has been observed in some sulfur pits maintained and operated by Saudi Aramco due to corrosion of concrete and steel reinforcement and spalling of concrete on the underside of the slab, resulting in severe reduction in load carrying capacity (Rahman et al. 2016). A partial collapse of roof has also been reported.

The sulfur pit under assessment at a natural gas production facility in Eastern Saudi Arabia has been in service for the past 18 years. It is inspected every three years and rehabilitation works of mechanical and structural components and conventional repair of the deteriorated concrete areas are carried out inside the pit. The maintenance of the pit has to be carried out in a limited time window and each day the plant is non-operational results in heavy financial losses. A major repair of these structures can be spread over several months span which has a huge economic impact. It is important to have an idea about the status of the roof slab of the pit from inside in order to plan the repairs ahead of the schedule, so that the repair work can be carried out in a short span of time within the planned shut down for maintenance.

The reinforced concrete structure has retaining wall on the periphery with a reinforced concrete roof slab. The pit is about 61.42 m in length and 14 m wide (Figure 1) with a clear height of 2.25 m. The roof slab is a flat plate supported on column 500 mm diameter in the center of the span and retaining walls at the edges. The walls (375 mm thick) and columns are supported on a raft foundation about 450 mm thick. The clear cover to the reinforcement on all exposed faces inside the sulfur pit is 75 mm. At the top surface of the roof slab the reinforcement is at a clear cover of 50 mm.

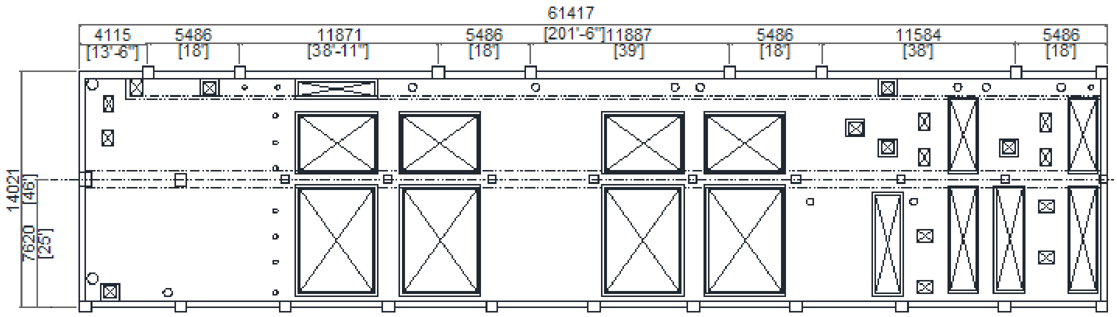


Figure 1: Typical top slab plan of the sulfur storage structure (sulfur pit)

The assessment of the pit was carried out in two phases. In the first phase, field investigations including visual survey and selected NDT (ACI 228.2R, 2013) of the roof slab of the sulfur pit were carried out with the sulfur pit in LIVE condition. Investigation of the roof of the sulfur pit prior to SRU Outage (On-Line Testing) is important in order to enable the management to establish the safety of the sulfur pit roof slab before the scheduled outage and develop a plan for repair and rehabilitation well in advance. The conventional hammer sounding survey was carried out to map the delaminated areas on the roof slab. This was followed by an ultrasonic impact echo tests on a large network of grid points on the top slab covering some of the inaccessible areas also. All accessible areas of the roof slab were marked and GRP readings were taken by moving the GPR along lines within the marked area. After the shutdown of the SRU, field investigations were carried out inside the pit in the second phase. Concrete core specimens were retrieved from inside of the tank from different locations on walls, foundations and top slab. Core samples retrieved from the structural components from inside and outside of the sulfur tank were used for strength and petrographic examination.

2 VISUAL INSPECTION AND DELAMINATION SURVEY

Visual inspection of the roof slab was carried out in the first phase together with hammer sounding to map the distresses including delamination and spalling. The visual survey also included photographic evidence of the distresses found in the structural components of the sulfur pit inside the pit in the second phase. The delamination survey on the top of the roof slab by hammer sounding indicated distress in several patches at the top of the roof slab as shown in Figure 2. A layer of new repair concrete with pea gravels, 25 mm thick, was identified on top of the roof slab of the sulfur pit at some locations. Shrinkage cracks were seen on the top slab.

Inside the pit a layer of thin coating exists on the ceiling of the roof slab, walls and the columns in the sulfur pit. The coatings are burnt, charred and have peeled off at several locations. Coatings on the columns have charred and turned black (Figure 3). No delamination or spalling of concrete observed in the ceiling of the sulfur pit. The coating may have inhibited the corrosion of steel in the top slab. A thick layer of sulfur is found attached to the coating at the junctions and near openings as seen in Figure 3. The walls of the sulfur pit show vertical cracks emanating from the bottom and going up to the top that can be attributed to thermal stresses. The concrete is very weak and friable and the concrete top layer could be removed easily in some portion indicating acid attack.

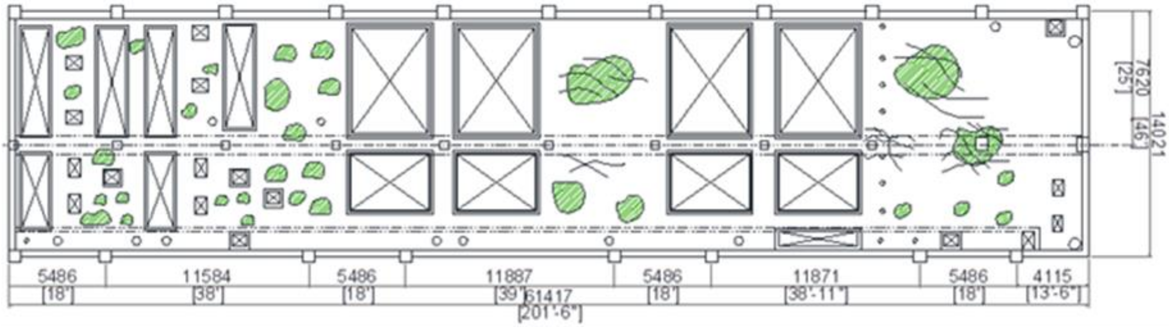


Figure 2. Cracking and delamination on the top side of the roof.

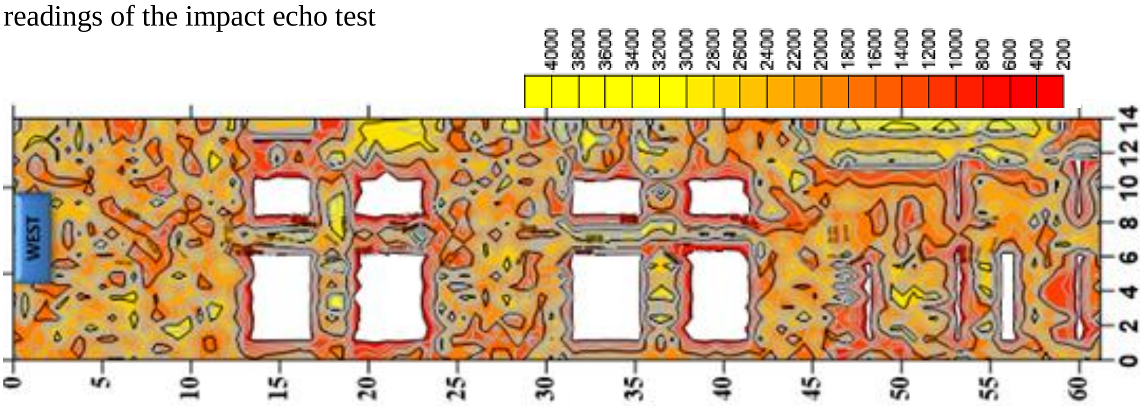
Figure 3. Delaminated coatings on the column and sulfur adhering to the surface at roof soffit.

A repair layer exists at the bottom of the walls at the junction between the walls and the base slab. The maintenance record for the pit shows that there was a leakage of sulfur and gasses from the joint between the base slab and the wall. The repair layer was probably placed to prevent the gas leakage. This repair was carried out within the first few years after the sulfur pit became operational. The repair layer has however, delaminated at many locations on the north and south walls and at one location on the East wall.

3 NON-DESTRUCTIVE TESTING OF CONCRETE

3.1 Ultrasonic Pulse Echo or Impact Echo

The results of impact echo tests at the top slab with the SRU in an operational state is shown in Figure 4. Irregularities in the concrete were identified based on the shear wave intensity. The ultrasonic pulse echo survey indicates that a significant portion of the roof slab has a weak concrete. Delamination of the top thin coating layer on the concrete could have masked the readings of the impact echo test

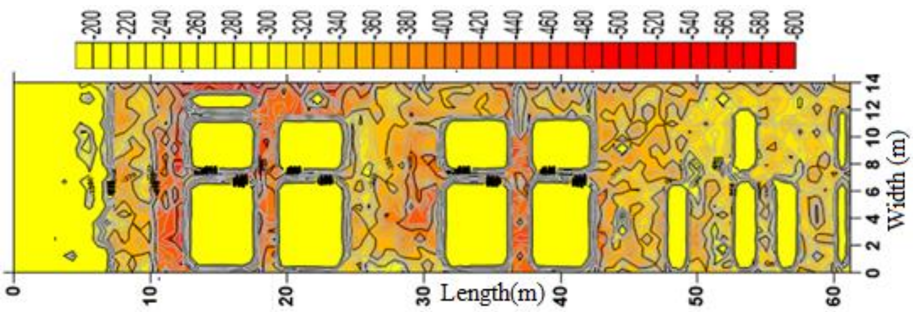


Speed (m/s)	Concrete Quality
X<2000	Bad
2000>X>3000	Moderate
3000>X>4000	Very Good

Figure 4. Impact echo readings at the roof slab of sulfur pits.

3.2 Corrosion Potential Measurements

Corrosion potential for detecting reinforcement corrosion and state of passivity of the reinforcing steel in concrete structures was based on ASTM C876 (2015). Potentials were measured at a grid spacing of 600 x 600 mm, in longitudinal and transverse directions on the top of the roof slab. This NDT test was carried out after shut down as in an operational state no breakout for reinforcement exposure was allowed. A reference electrode was placed on the concrete surface, which is connected via a high impedance Voltmeter (> 109 Ohms) to the reinforcement cage. Corrosion potential mapping for the roof slab is shown in Figure 5. It can be seen that the corrosion potential at most of the roof slab is within threshold limit. Limited corrosion was identified around openings.



Potential mV	Corrosion Probability
<-350	> 95 %
-200 to -350	approx. 50 %
>-200	< 5 %

Figure 5. Corrosion potential mapping.

3.3 *Ground Penetration Radar Survey*

Ground Penetrating Radar (GPR) is an effective method for mapping the subsurface anomalies up to a depth of 5 meters (ASTM D 6432, 2011). The GPR employed in this study is a high frequency 1600 MHz GPR, which can penetrate into the concrete to a depth of 0.5 meters. GPR was also used to locate reinforcement in the concrete slab before extracting cores. The GPR scans 2D and 3D were carried out at accessible places on the top of the slab. A large area of the slab has restricted accessibility due to the pipes and the process equipment. GPR scan were performed in all accessible areas. These scans were taken using identical settings for the GPR equipment, data processing procedures, and scanning location to eliminate the impact of any parameter other than the concrete quality. Dielectric constant was assumed as 6.0, which corresponds to that of a dry concrete.

A 2 mm thick fiber-reinforced cementitious layer exists on the top of the slab. The cover to reinforcement is about 120 mm as can be seen in Figure 6. The thickness of concrete cover for the top rebar layer is approximately 130 mm from the top. The depth of bottom rebar layer is about 320 mm. The total depth of the roof slab is about 420 mm as obtained from the GPR data. The top reinforcement location is clear but the bottom reinforcement location can only be judged. It can be seen that reflection from good reinforcing top steel is very sharp and some weak reflections is clear from the good bottom steel. On the other hand, the corroding reinforcing steel completely blankets the area at the bottom of the element using GPR. It can be seen that the bottom reinforcement cannot be identified at locations where the top bars are located.

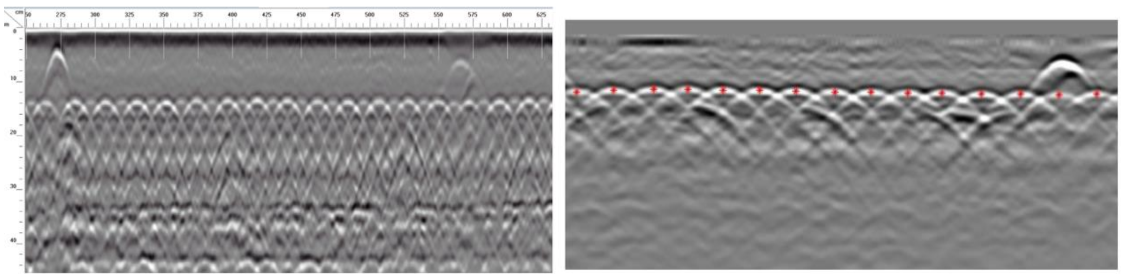


Figure 6: GPR indicates a thin layer of fiber-reinforced cementitious layer on the top of slab with a cover of about 125 mm.

The GPR survey shows severe to moderate corrosion of reinforcing steel on the North side of the slab towards the Eastern end. Apart from this area, corrosion of steel identified through radar grams can be seen in a number of patches around the openings as well as in some cases away from it. The GPR results indicate that a large portion of the scanned area of the slab shows sound concrete. Only about 5% shows signs of severe corrosion. Moderate corrosion is significant particularly around openings, the northern end and the other edges.

4 LABORATORY INVESTIGATIONS ON CONCRETE CORE

4.1 Cores from Areas Inside the Sulfur Pit

Figure 7 shows the concrete cores obtained from inside the pit (ASTM C42, 2018) . In the core from the base slab (left) about 2.5 to 3 cm of the core appears to be affected with sulfur penetrating into the concrete. The cores obtained south wall from bottom (middle) and top (right) shows the acid attack on the concrete surface. The penetration of acid attack up to 4 cm can be seen in south wall core obtained from zone affected by acid vapors. Dark color concrete core can be seen in the zone which remains immersed in sulfur. In the south wall top core, the surface layer is weak and friable. The cores obtained from the North wall from bottom and top shows that the concrete in top layer in the North wall has lost its strength and was easily broken. The bottom part of the North wall has been repaired with a 250 mm thick repair concrete as is evident from the core. The acidic vapor appears to have penetrated to a depth of 800 mm in the vapor zone on the top of the North wall.

Figure 7. Concrete core retrieved from north wall top (left) and bottom (right).

4.2 Compressive Strength of Concrete

In the project specifications Type-I cement was specified with a minimum compressive strength required after 28 days of curing was 5000 psi (35 MPa). Compressive strength tests were condcuted on concrete cores obtained from the sulfur pit (ASTM C39, 2018). The actual compressive strength of concrete was found to be very high in the concrete submerged in molten sulfur as compared to above the sulfur level. The strength of about 86 MPa (12,500 psi) was found in all walls at the bottom. This may be due to the crystallization of sulfur in the concrete pores. In the walls of the sulfur pit, the average compressive strength of concrete retrieved from top of three different walls of the sulfur pit was about 35.8 MPa. The strength of concrete extracted from the foundation was 42.8 MPa. Two concrete cores from the roof slab were extracted at different locations, one of the cores showed 24.4 MPa compressive strength and the other was lower at 21.7 MPa.

4.3 Petrographic Analysis of Concrete

Two specimens, one extracted from the West wall top level in the vapor zone and the other extracted from the top slab were subjected to petrographic examination according to ASTM C856 (2018). The concrete mix has nominal 19mm, crushed limestone/dolomite coarse aggregate and quartzitic sand fine aggregate, bound by a probable Portland-type cement matrix. The concrete is apparently well mixed, exhibiting good compaction. The excess voidage is about 0.5%. The petrography of concrete core from the slab shows that the acidic sulfur vapors have affected the soffit of slab. A dark grey color change of the cement matrix is the result of chemical alteration and some degree of polymerization in the concrete mix. The micopores in the cement matrix are in general infilled by sulfate minerals. Several parallel microcracks that were completely infilled by sulfate minerals were observed in the top layer of the concrete. Figure 7 shows a selected core and the thin concrete section for microscopic examination.

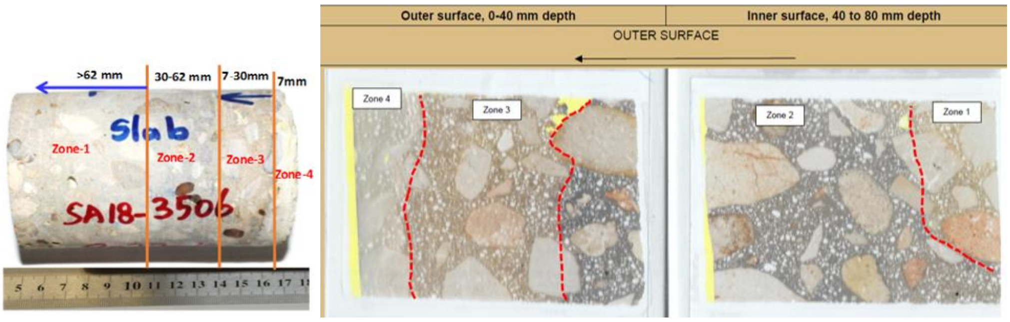


Figure 8. View of thin section showing zones of alteration within the concrete

It can be seen from the figure that the concrete in Zone 1 at the interior of the core is sound. In the outer most layer (Zone 4) there is an abundant evidence of sulfate attack in terms of abundant cracks sub-parallel to the outer surface infilled by sulfate minerals, air voids infilled by sulfate minerals, partial replacement of the cement matrix by sulfate minerals and layered deposits of sulfate minerals within and adjacent to coarse aggregate particles.

In the second zone from the surface of the ceiling (7 – 30 mm) there is a moderate evidence of sulfate attack, sporadic air voids microcracks infilled with sulfate minerals. Alteration of the cement matrix and increased densification is also observed. The third zone from the surface extending from 30 mm to 62 mm shows minimal evidence of sulfate attack, sporadic air voids microcracks infilled with sulfate minerals. Alteration of the cement matrix and increased densification can be observed.

5 CONCLUSIONS

Based on the investigations carried out it can be concluded that the overall condition of the roof slab can be rated as "Good" and those of the walls inside the pit as "Fair". The following are the major findings from the study:

1. A layer of new repair concrete with pea gravels, 25 mm thick, exists on the top of the roof slab of the sulfur pit at some locations. The concrete strength of the slab is only 23 MPa, whereas the specifications called for 35 MPa at 28 days. Fiber reinforced cementitious coating was found in some portions of the top slab having a thickness about 2 to 5 mm.

2. The ultrasonic pulse echo survey indicates that a significant portion of the roof slab has a weak concrete. Delamination of the top thin coating layer on the concrete probably masked the readings of the impact echo test. In most of the areas on the roof slab, half-cell corrosion potentials (HCP) recorded were less negative than the threshold value of -350 mV, indicating that the reinforcing steel in these areas is still in passive state of corrosion.

3. The GPR results shows that only about 5% of the top slab reinforcement shows signs of severe corrosion. Moderate corrosion is significant particularly around openings. Concrete cover is found to be very high (about 125 mm) at the top. The thickness of slab is 420 mm (drawings shows 375 mm). The GPR study on LIVE sulfur pit does not reveal the condition of the reinforcement at ceiling inside the pit. GPR gives robust indication of corrosion of reinforcement at the top of the slab. If the reinforcement at top is corroded, the bottom reinforcement is completely masked.

4. A layer of thin layer of coating, which is burnt, charred and have peeled off at several locations exists on the ceiling of the roof slab, walls and the columns in the sulfur pit. No delamination or spalling of concrete observed in the ceiling of the sulfur pit. The coating may have inhibited the corrosion of steel in the top slab.

5. Very high strength 86 MPa concrete in all walls at the bottom in the sulfur-immersed zone. Movement of liquid sulfur front into the concrete walls although increases the compressive strength is destructive by generating crystallization pressure. The South and West Walls have concrete strength of 30 MPa and 33.5 MPa in the sulfur vapor zone, whereas, the North wall and base slab concrete strength is 43 MPa.

11. The petrography of concrete core from the slab shows that the acidic sulfur vapors have affected the soffit of slab. Top 10 mm seems to be heavily affected. Petrography shows weak, friable and cracked concrete in top 7 mm. There is a moderate level of sulfur penetration in the slab, up to a depth of 30 mm with voids and microcracks filled with sulfur. The maximum depth to which the sulfur has infiltrated into the slab is up to 60 mm.

6 ACKNOWLEDGMENTS

The support provided by the Center for Engineering Research, Research institute at King Fahd University of Petroleum and Minerals. The study was conducted for Saudi Aramco and their support for this study is acknowledged.

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