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Effects of alum, soda ash, and carbon dioxide on 40–50 year old concrete wastewater tanks

Abstract: Concrete is among the foremost used construction materials around the world, however, there is limited information to determine how aging concrete is affected by chemicals. Concrete is used in the construction of domestic and industrial infrastructure including walls, beams, roof slabs, pipes and drainage systems. With increasing industrialization, chemicals are continuously released contributing to concrete degradation. Sulfuric acid is one of the most detrimental chemicals to concrete, yet it is commonly used in most industries. The effects of carbon dioxide, alum, and soda ash on 40–50 year old concrete structures were determined. Results showed the presence of Fe^{3+} ions with a mean concentration of 3.24 ± 0.02 mg/L in the residuum on the alum tank. This was due to the slightly acidic alum solution reacting with calcium hydroxide and iron in the concrete matrix over years thus depriving concrete of its binding power. The high amount of soda ash, a strong base, corrodes the concrete walls and surfaces hence creating cracks on the concrete matrix. Carbonation effects brought about by carbon dioxide were also observed at the time of the study.

Keywords: alum; carbonation; concrete; degradation; reinforced concrete.

1 Introduction

Concrete is among the most widely used construction material around the world [1]. It is prepared by mixing cement, water, and aggregate such as sand and gravel in specified ratios. Since aggregate is mostly considered to be chemically inert in the matrix, the chemistry of concrete mostly lies in the hydration of cement. Portland cement is made up of four main compounds: tricalcium silicate ($3CaO{\cdot}SiO_2$), dicalcium silicate ($2CaO{\cdot}SiO_2$), tricalcium aluminate ($3CaO{\cdot}Al_2O_3$), and a tetra-calcium aluminoferrite ($4CaO{\cdot}Al_2O_3Fe_2O_3$) [2, 3]. The raw materials for manufacturing cement include limestone

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($CaCO_3$), silica (SiO_2) alumina (Al_2O_3), and ferrous oxide (Fe_2O_3). These materials are dried, heated, and fed to a rotating kiln where they react at very high temperatures to form tricalcium silicate ($3CaO.SiO_2$), tricalcium aluminate ($3CaO.Al_2O_3$), and tetra calcium aluminoferrate ($4CaO.Al_4Fe_2O_3$). Calcium oxide is the most abundant oxide in cement with 60–65% abundance, followed by silicate at 17–25%, aluminate at 3.0–8%, and ferrous oxide at 0.5–6% [2–4]. During hydration of cement, water reacts with calcium oxide in cement to form calcium hydroxide ($Ca(OH)_2$), a major constituent of concrete paste, which makes concrete alkaline and highly vulnerable to acid attacks [5–7].

To ensure that the concrete reinforcement is firm, steel rods/bars are incorporated in it to make ferroconcrete [8]. Iron being a constituent of steel is susceptible to acid and alkali attacks [4, 7]. Alum ($Al_2(SO_4)_3.nH_2O$) is employed in wastewater treatment plants as a coagulant to realize coagulation, flocculation, and sedimentation; processes that aid clarification of water [9]. It is prepared by dissolving aluminum sulfate granules typically in concrete holding tanks which provide the requisite capacities for wastewater treatment plants. Alum dissolution produces vitriol which reacts with concrete (Eq. (1)). Vitriol is among the foremost deleterious acids to act on concrete; it reacts with lime to supply gypsum ($CaSO_4$) which causes a volume increase [5, 8, 10]. Ordinary hydraulic cement has minimal resistance to acid attacks and is unable to carry up against any solution with a pH value of less than three [7]. Gypsum further reacts with calcium aluminate hydrate to produce ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) which causes inner pressure within the concrete resulting in the formation of cracks [6, 11, 12]. Ultimately, the corroded concrete loses its mechanical strength that contributes to more cracking, spalling, finally resulting in destruction.

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2SO_4 \quad (1)$$

Carbonation is a natural phenomenon that occurs when carbon dioxide from the atmosphere comes into contact with concrete structures, penetrating through them toward the interior [10, 11]. It is a slow process that depends on the concentration of carbon dioxide and natural humidity variation in the target environment and follows Eq. (2). Water from the atmosphere dissolves carbon dioxide resulting in the formation of carbonic acid which reacts with concrete as described in Eqs. (3) and (4). The calcium hydrogen carbonate ($Ca(HCO_3)_2$) formed reacts with calcium hydroxide to regenerate calcium carbonate (Eq. (5)). Carbonic acid decreases the hydrogen ion potential of the system due to the H^+ ions present. As a result, the C-S-H and anhydrous components in the cement paste dissociates in the form of amorphous silica making the concrete highly porous and brittle [11, 13]. Thus, high levels of carbonation can result in loss of structural integrity of the concrete material.

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \quad (2)$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow Ca(HCO_3)_2 + H_2O \quad (3)$$

$$H_2CO_3 + CaCO_3 \rightarrow Ca(HCO_3)_2 \quad (4)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \quad (5)$$

Concrete-alkali reaction proceeds as reactive aggregates attack the alkaline components in cement. The reaction causes a volume increase in concrete thus creating tension and swelling in walls. Alkali reactions are responsible for irregular cracks in concrete as well as a reduction in mechanical properties of up to 50% [10]. Sodium carbonate is employed to boost the pH of water during the treatment process. As mentioned earlier within the case of alum, sodium carbonate is additionally prepared by the dissolution of granules in concrete tanks as described by Eqs. (6) and (7). Sodium bicarbonate reacts with lime to make caustic soda and carbonate as shown in Eq. (8)

$$Na_2CO_3 + H_2O \rightarrow NaOH + NaHCO_3 \quad (6)$$

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH \quad (7)$$

$$2NaHCO_3 + Ca(OH)_2 \rightarrow 2NaOH + Ca(HCO_3)_2 \quad (8)$$

This study seeks to determine the effects of alum, soda, and dissolved carbon dioxide on 40–50 year old concrete tanks used in a wastewater treatment plant. The concrete tanks were observed for wear as well the determination of ion concentrations in solutions held in the tanks.

2 Experimental

To determine the effect of the discussed chemicals on aging concrete, water and sludge samples were collected from a 50 year old wastewater treatment plant and analyzed for iron, aluminum sulphate, and calcium carbonate concentrations. The samples collected included rainwater, raw water entering the treatment plant, wastewater after the several treatment stages (Treated water 1, 2, and 3), desludge, stalactite, and stalagmite like protrusions in concrete tanks, and residuum on alum and soda tanks. All samples were analyzed according to procedures reported by Totan et al. [14]. Solid samples were dissolved in nitric acid while water samples were analyzed without further pretreatment [13]. All samples were stored in sealed sample bottles and refrigerated at 4 °C. Solutions of required concentrations were prepared by performing serial dilutions from the relevant stock solutions. Sulphate ion concentration was determined spectrophotometrically on a UV–VIS Spectrometer model DR 5000R while aluminum concentration was determined by complexation with ascorbic acid followed by UV–VIS analysis. Iron concentration was determined using atomic absorption spectrophotometry on an AAS model AA 6300.

3 Results and discussions

Concrete structures are used for the construction of permanent buildings and structures due to their durability. These structures are however affected by chemical and environmental factors which adversely affect their structural integrity [10]. Aggressive chemical environments such as those found in chemical dissolution and storage tanks in wastewater treatment plants can cause degradation of concrete structures as the chemicals tend to react with calcium hydroxide in cement a major component of concrete [10, 15]. In addition, aluminum ions may come into contact with iron bars in the concrete and cause galvanic corrosion. The corrosion can cause expansion of the concrete and consequent cracking of the hardened concrete [5]. Effects of degradation on iron concentration and physical observation of 40–50 year old concrete tanks used for handling of liquids (alum and soda) in a wastewater treatment plant indicated wearing of the tanks. The worn out concrete indicated exposure of embedded steel bars and their subsequent corrosion. The tanks used for dilution of alum and soda solution were worst affected as shown in Figure 1. Figure 1(C) shows a 50 year old tank with degraded concrete exposing the embedded steel bars. As seen, the steel bars are corroded resulting in the dissolution of iron in the solution.

The pH of alum was determined to be 2.5 while that of soda ash solution was determined to be 12.5. The low pH of alum solution results from its dissolution producing sulfuric acid as a by-product that reacts with calcium hydroxide in concrete as previously discussed [5]. Soda solutions' basic nature results from sodium hydroxide and sodium hydrogen carbonate. The highest degradation is therefore attributed to alum and soda ash solutions due to their highly acidic and basic nature, respectively [5, 15].

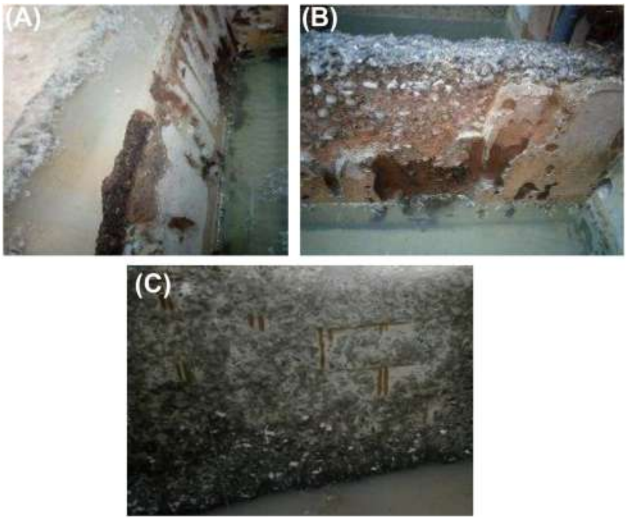

Figure 1: Wastewater tanks. (A) Soda ash, (B) alum solution tanks, and (C) alum tank showing worn concrete worn exposing embedded steel bars.

3.1 Iron (Fe^{3+}) concentration

To determine the concentration of iron in the tank, water samples were collected and analyzed for Fe^{3+} concentrations alongside treated water from the wastewater treatment process. The results obtained for Fe^{3+} concentrations in Figure 2 indicate that the sample obtained from the residuum on the Alum tank had the highest Fe^{3+} concentration (3.24 ± 0.02 mg/L) followed by the residuum on the soda ash tank (0.66 ± 0.06 mg/L). Comparing these with the Fe^{3+} ions content in the raw water sample (0.11 ± 0.01 mg/L) shows that iron is introduced into the water within the plant. Since iron is not added during the wastewater treatment process and raw water did not contain significant amounts of iron, the source of iron in the solution is attributed to the degradation of steel bars after concrete degradation (Figure 1).

3.2 Aluminium concentration

The desludge was found to contain 70.00 ± 0.00 mg/L of Al^{3+}. This could be attributed to the fact that alum was used in the wastewater treatment plant as a coagulant (Figure 3). The spent alum settles as sludge at the bottom of the clarifiers and is later discharged as desludge. The concentrations of Al^{3+} in the residuum behind the concrete tank, soda tank, and in raw water were however insignificant. This indicates that aluminum does not seep through the concrete matrix thus does not displace calcium from the concrete matrix.

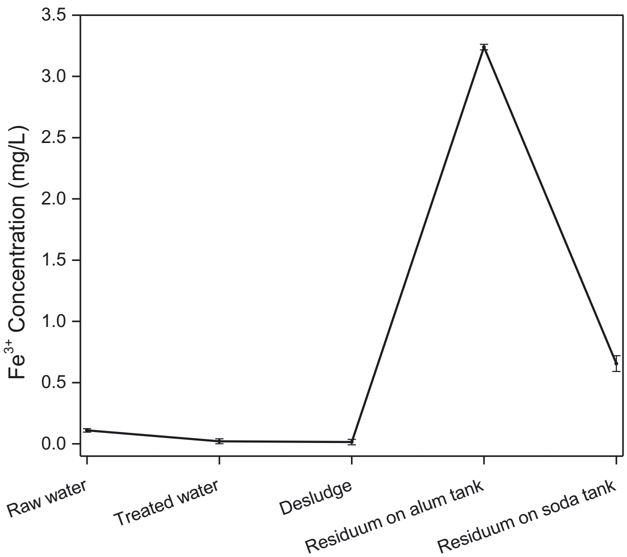

Figure 2: Concentration of Fe^{3+}ions (mg/L) in samples from various stages in the wastewater treatment plant.

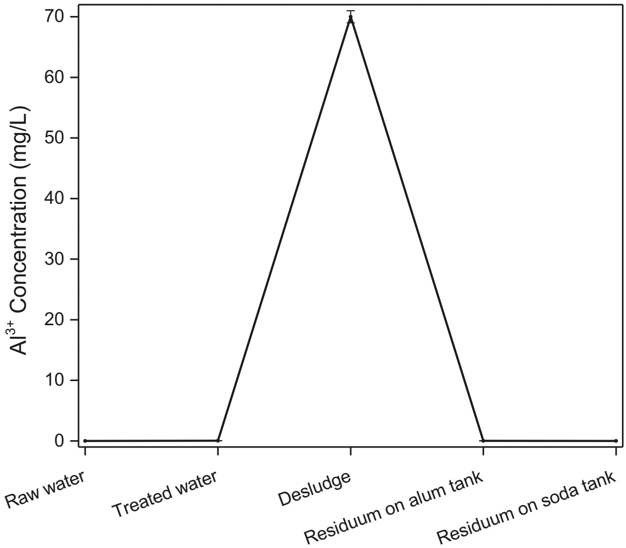

Figure 3: Concentration of Al^{3+} ions in water samples.

3.3 Sulphate ion concentrations in the samples

Figure 4 shows that sulfate ions from calcium sulfate were abundant in the residuum from the alum tank. A mean concentration of 316.67 ± 11.55 mg/L of sulfate ions was obtained in the desludge. The high sulfate ions concentration was an indication that there was a reaction between calcium hydroxide in the concrete with sulfuric acid

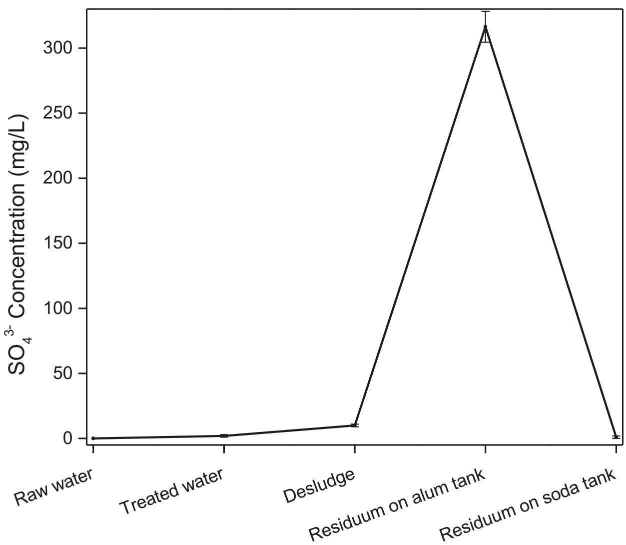

Figure 4: Sulfate content in selected samples in the wastewater treatment plant.

produced by the dissolution of alum. The formed calcium sulfate was later deposited in seepage cracks hence collected as residuum on the tank walls since Portland cement is expected to contain a minimal amount of sulfates present in gypsum ($CaSO_4{\cdot}2H_2O$) [3]. Sulfate ions from alum solution, therefore, react with calcium ions from concrete to form derived gypsum and can react with tricalcium aluminate (in concrete) to form ettringite, $3CaO.Al_2O_3.3CaSO_4.32H_2O$, aluminum sulfate is able to react with calcium hydroxide to form ettringite without first forming tricalcium aluminate [6]. Continued reaction keeps on disintegrating concrete and as this happens cracks/holes develop on the concrete structures as shown in Figure 1(B).

3.4 Effect of carbonation on concrete tanks

Figure 5 showed the formation of stalactite and stalagmite-like formations in soda ash dissolution tanks on its roofs and floors. This could be attributed to the carbonation of concrete. The process of carbonation is continuous with CO_2 diffusing through concrete reacting with lime to make carbonate hence wearing the surface [16–18]. The dissolution of calcium hydroxide in the concrete leads to increased capillary porosity and loss of cohesion in the concrete matrix [18]. This weakens the cement paste to aggregate bond leading to the formation of cracks and disintegration or destruction of the concrete structure when subjected to pressure. As this process reaches the depth of concrete, formed calcium carbonate falls from the top resulting in the formation of stalactites and stalagmites. The process utilizes the calcium hydroxide in the concrete matrix therefore degrading it [19].

The mechanism for the carbonation of the concrete wall is similar to that resulting in the formation of stalagmites and stalactites in limestone caves (Figure 5). The analysis of their composition revealed that 92.67% of their composition is $CaCO_3$. This indicated that concrete has undergone a roof-carbonation process to form $CaCO_3$. Rainwater from the wastewater treatment plant was determined to be slightly acidic at

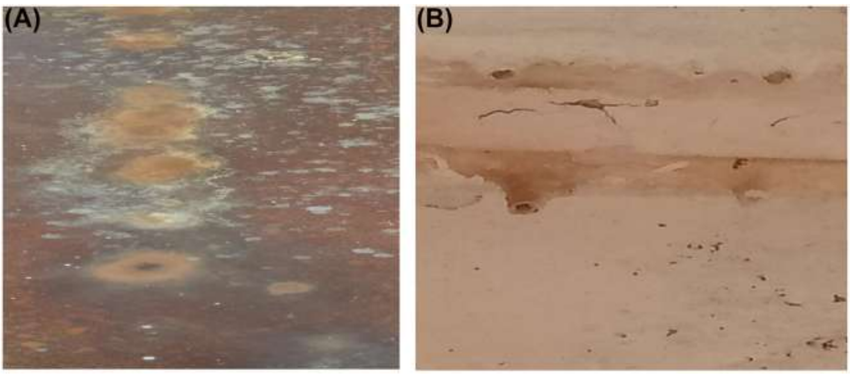

Figure 5: Formation of stalactites and stalgmatites in concrete tanks. (A) Stalactite and (B) stalagmites formed in concrete tanks.

a pH of 6.75 due to the dissolution of atmospheric CO_2. Concrete's compressive strength and carbonation depth are significantly influenced by its humidity, temperature, and carbon dioxide concentration [15, 17–21]. At humidity of approximately 70%, the carbonation depth is maximized since the chemical reaction and transmission coefficients are proportional to ambient temperatures [15]. The carbonated concrete wall was found to have 99.5% by mass $CaCO_3$. This result indicates that the process of carbonation is well occurring on the walls of concrete structures utilizing calcium hydroxide in the concrete matrix. In pronounced cases, the effects may leave the concrete bond weak and may result in accidents [22].

4 Conclusions

Alum is a strong acid that highly affects concrete. The acidity is due to its reaction with water to form Sulfuric acid whose pH was found to be less than 3. The Sulfuric acid reacted with calcium hydroxide in the concrete to form calcium sulfate hence wearing the concrete tanks. The wearing process continued and the iron (steel) bar in the concrete matrix was exposed. The high mean concentration levels of Fe^{3+} (3.24 ± 0.02 mg/L) obtained in the residuum on the alum tank is a clear indication that the exposed iron bars reacted with the acid formed during the dissolution of alum in the alum tank. This study, therefore, indicates that deterioration of concrete by alum is possible. Soda ash solution was found to be highly basic with a pH above 12. This high pH resulted in the corrosion of the concrete tanks' floors and walls forming holes and cracks hence reducing the binding strength of the aged concrete. The worn concrete exposed the reinforcing steel bars to soda ash chemical attack. Therefore, the soda ash solution in aged concrete tanks was observed to wear the concrete and reduce its efficiency.

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