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Corrosion in Concrete Structures of the Leyte Geothermal Production Field, Philippines: Characterization and Implications

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ABSTRACT

Corrosion was documented in two concrete structures in the Leyte Geothermal Production Field (LGPF), Philippines. Deterioration of the cement matrix to a weak and powdery state left the rock aggregates protruding out of the concrete surfaces of the rock muffler in South Sambaloran and of spray tower posts in the Upper Mahiao Zero Effluent Disposal System (UM ZEDS). These field observations were initially noted in September 2003 in the rock muffler, and during the October 2004 Annual Preventive Maintenance Service (PMS) of the UM ZEDS.

Various laboratory analyses such as phenolphthalein test, X-ray diffractometry (XRD), and scanning electron microscopy (SEM-EDAX) indicate that the deterioration of the rock muffler structure was mainly caused by attack of sulfuric acid (H_2SO_4) formed from H_2S in the condensed steam. Sulfuric acid reacts with portlandite in the cement matrix, which becomes weak and powdery, leaving the aggregates exposed as the matrix is gradually removed from the exposed surface of the concrete. On the other hand, the soft friable nature of the UM ZEDS spray tower posts, and the development of secondary calcite in the cement matrix suggest that the concrete was already attacked by carbonic acid formed by dissolved CO_2 in the power plant effluents. Apart from decomposing the cement paste, carbonation also lowers the pH of concrete hastening corrosion of reinforcing steel bars in the spray tower posts.

To minimize acid attack on other concrete structures in LGPF using the South Sambaloran rock muffler as a case study, it was recommended to modify concrete composition to reduce content of chemicals vulnerable to aggressive ions. Portlandite content must be kept low and blended cements with high amounts of fly-ash, pozzolan, or blast-furnace slag must be used. For the UM ZEDS, the spray tower posts were resurfaced with special cement mix of high density blended with fly-ash. In addition, posts and the basin were jacketed with molded high-density polyethylene plastic that is both durable and resistant to corrosion attack.

1. INTRODUCTION

Concrete deterioration was investigated in two structures in the Leyte Geothermal Production Field, Philippines, namely, the rock muffler in South Sambaloran Sector, and the spray tower posts of the Zero Effluent Disposal System (ZEDS) in Upper Mahiao. These structures showed similar physical characteristics of a generally weakened cement matrix.

The rock muffler is used for emergency disposal of steam during power plant tripping, and disposal of excess steam during the daily power plant load reduction. It is used for an average of 2-3 hours (non-continuous) per day during the daily load reduction. The rock muffler was constructed in 1997 and commissioned in July 1998. The damage was documented in September 2003 and was manifested in the cement matrix turning powdery white and easily removable. As a result, the rock aggregates were exposed, protruding out from the damaged cement matrix.

The Zero Effluent Disposal System (ZEDS) was built in December 2002 for disposal of steam condensates coming from the Upper Mahiao power plant. During the October 2004 annual Preventive Maintenance Service (PMS) in Upper Mahiao, concrete corrosion was initially documented in the spray tower posts of the ZEDS. The cement matrix of the concrete posts was transformed into a soft and friable powder consequently exposing the rock aggregates. The spray tower posts were eventually rehabilitated during the October 2005 PMS.

Corroded concrete samples were collected from both the rock muffler and spray tower posts, and subjected to various types of analysis to fully identify the components, and describe the features and microstructures. These analytical methods sequentially consisted of visual or megascopic analysis, phenolphthalein staining tests, stereo optical examination, petrographic optical microscope analysis, and scanning electron microscopy – energy dispersive spectrometry (SEM-EDAX) together with X-ray diffractometry (XRD) for compositional verification. All petrologic examinations were done at the Petrolab, EDC, Philippines. Other analyses of the rock muffler sample were conducted by the Holcim Group Support Ltd. in their laboratory in Im Schachen, Holderbank, Switzerland. On the other hand, phenolphthalein test of the spray tower post was carried out at the EDC Petrolab; while SEM-EDAX at De La Salle University's Science and Technology Research Center, Metro Manila, Philippines.

This paper presents results of the various laboratory analyses, describes in detail the cause of corrosion of the South Sambaloran Rock Muffler and Upper Mahiao spray tower concrete posts, and proposes mitigating measures to prolong life of the concrete structures.

2. ROCK MUFFLER – SOUTH SAMBALORAN

2.1 Description of the Environment

The reinforced concrete elements are exposed to extreme environments characterized by a wide range of temperatures (180 °C when geothermal steam is fed, and ~26 °C in the absence of steam). The entire structure is located in open space, and exposed to both sun and rain.

Significantly, the geothermal steam is rich in H_2S and CO_2, producing acidic condensates as shown in the typical chemistry of steam condensate coming out of the muffler (Table 1).

Table 1: Typical Chemistry of Steam Condensates. Rock Muffler, South Sambaloran

Component	Value
Cl	1.02 mg/l
SO4	<10 mg/l
H2S	102 mg/l
TCO2	411 mg/l
pH	4.5 - 5.5

Using EN Standard 206 as a basis, the combination of chemicals in the rock muffler steam classifies the structure to Exposure Class XA3 corresponding to a "highly aggressive chemical environment". This is further aggravated by the high and varying temperature and moisture conditions prevailing in the immediate environment.

2.2 Macroscopic Analysis

The exposed surface of the sample showed removal of the cementitious matrix, leaving the aggregates exposed (Fig.1). Another rough surface was presumably the result of an existing crack. Remnants of a corroded steel bar was observed at the other side of the sample opposite to the exposed surface (Fig. 2).

The sample was initially saw-cut dry along a plane perpendicular to the exposed surface, and also perpendicular to direction of the steel bar. The freshly obtained section was sprayed with phenolphthalein solution to measure the carbonation depth. This test measures the transition between the alkaline pH zone (pink color) and the neutral or even acid pH zone (non-colored). In the case of the rock muffler, the loss of alkalinity might be due, not just to carbonation, but also to other forms of chemical reactions.

Figure 1: Rock Muffler sample shows removal of cementitious matrix, leaving aggregates exposed.

The phenolphthalein test revealed a layer (ca. 5 mm deep) of non-alkaline concrete at the exposed surface (Fig. 3). A brownish rim about 1 mm deep was also noted inside the non-alkaline zone. The structure of the concrete appeared dense with a relatively low content of coarse aggregate particles, which are also relatively small in size, generally not more than 10 mm. Few cracks were observed.

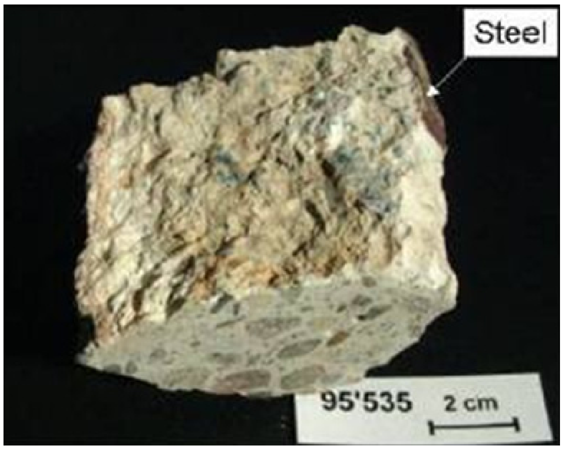

Figure 2: Remnants of corroded steel bar at the other side of sample

2.3 Analysis of the Concrete Microstructure

Two polished sections were prepared, one of the exposed surface zone and another one of the zone surrounding the corroded steel bar. Both sections were oriented perpendicular to the exposed surface and to the corrosion layer.

SEM-EDAX analysis of polished sections of the crumbly top layer exposed to aggressive atmospheric conditions showed the predominance of gypsum and anhydrite (Fig. 4). Crack formations within the investigated zones were rarely observed. The large aggregate grain in the lower right corner of Figure 4 displays an enrichment of sulfur along its boundaries. This zone was further investigated by elemental mapping. The sulfur in these zones is again present as secondary formations of gypsum or anhydrite. A spot analysis of a single, sulfur- containing crystal in this zone displays no other relevant elements besides Ca and S (Fig. 5). Some of the gypsum crystals display minute layers of an Al-containing phase accompanied by Ca and S. These layers are most probably transformation products of gypsum into ettringite or monosulphate. Gypsum and anhydrite are however strongly dominant as S-bearing phases in this zone. Pores in the top 10-mm layer exposed to acid attack simply contain Ca and S, which are again indicative of gypsum or anhydrite.

Figure 3: Phenolphthalein test

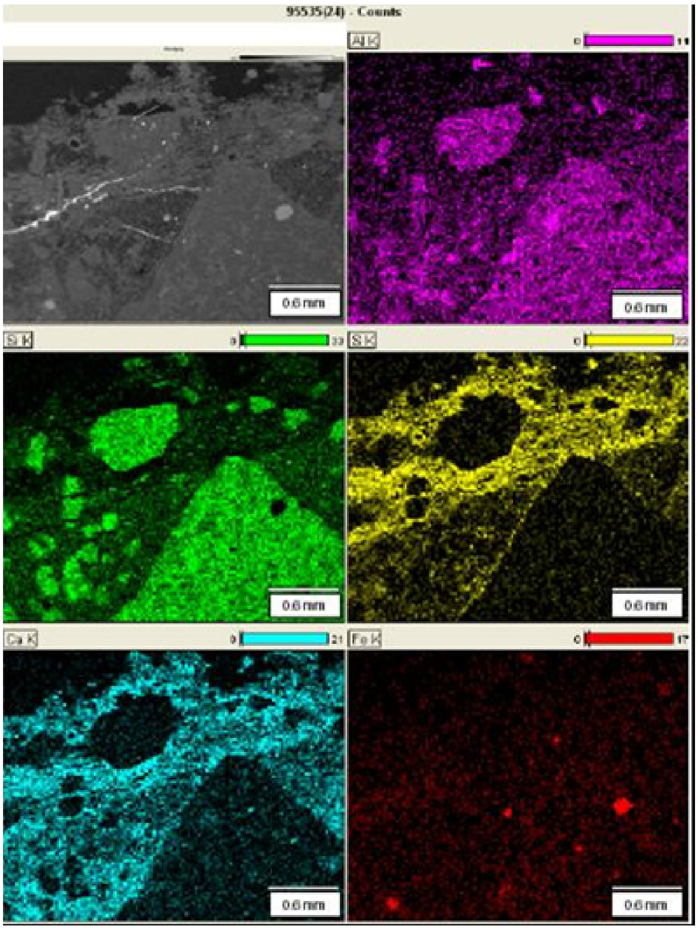

Figure 4: SEM-EDAX mapping of top layer shows enrichment in S and Ca.

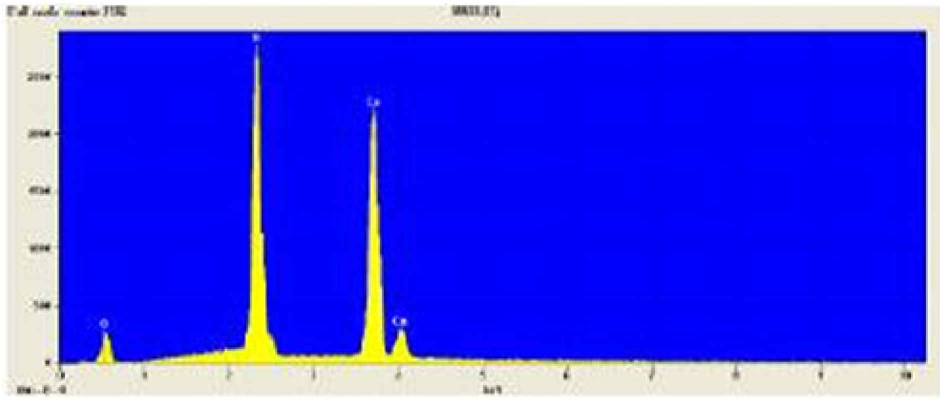

Figure 5: Spot analysis of secondary formed gypsum or anhydrite in top layer.

Deeper inside the concrete, approximately 10 mm from the corroded steel bar, a white powdery seam was observed around a larger aggregate which protruded from the crack surface. Based on XRD analysis, this seam consists of secondary formations of calcite and aragonite (Fig. 6).

The corrosion products of the steel bar were analyzed for infiltration products of salts. Small amounts of chlorides were identified besides iron oxides. The presence of other oxidation states of iron or of iron hydroxides cannot be excluded. Zones adjacent to the corrosion products are rich in Ca and Si as expected from hardened cement paste. Enrichments of Cl- or S-containing salts were not detected by EDAX mappings in this zone.

3. SPRAY TOWER POSTS – UPPER MAHIAO ZEDS

The Upper Mahiao ZEDS is similarly located in open space and exposed to variable weather and temperature conditions like the rock muffler. The chemistry of the UM ZEDS sprayed condensate, taken at the power plant interface (Table 2) shows elevated dissolved CO_2 likewise resulting in acidic condensates.

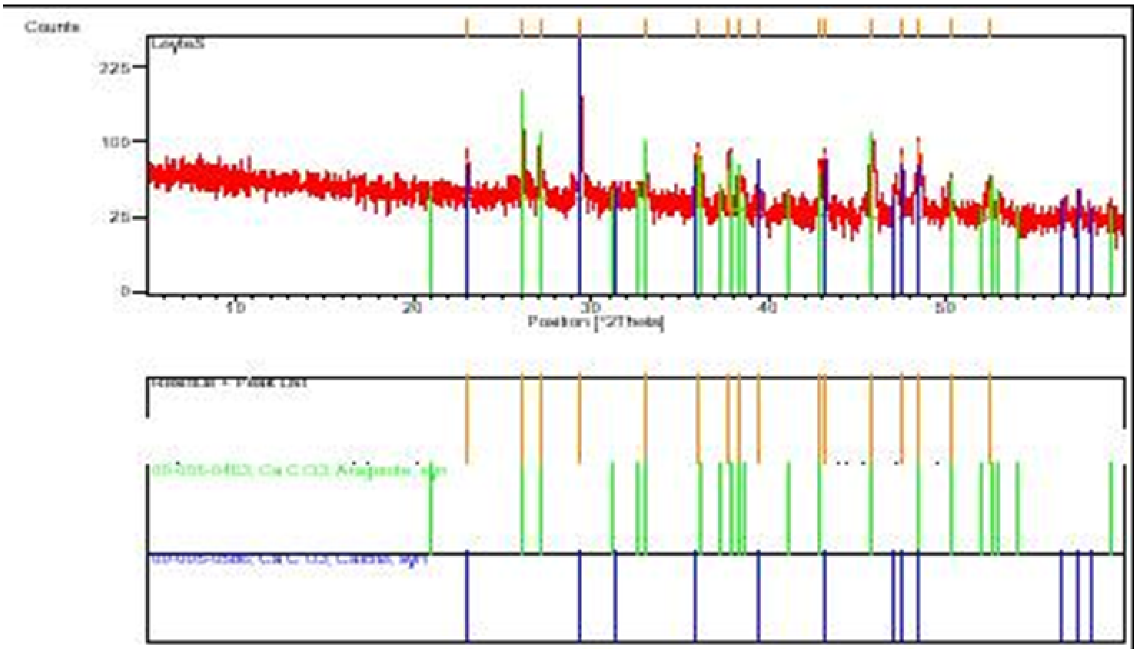

Figure 6: XRD analysis shows secondary calcite and aragonite around aggregate 10 mm from steel bar

Table 2: Chemistry of LGPF UM ZEDS

Component	Amount (ppm)
CO2	241
H2S	12.2
HCO3	31.4
Dissolved O2	0.14

Figure 7: Corroded concrete posts of the Upper Mahiao spray tower.

Figure 8: Rock aggregates protruding out of the corroded concrete surface.

3.1 Macroscopic Analysis

A rectangular slab was saw-cut from one of the corroded posts of the Upper Mahiao spray tower during the October 2005 annual preventive maintenance service in LGPF (Fig. 7). The sampling was timed during this period when the posts were accessible and the infrastructure was undergoing rehabilitation work.

The concrete slab showed an orange-colored oxidized surface. Its cementitious matrix has been removed leaving the aggregates exposed and protruding out of the concrete surface (Fig. 8).

The concrete slab was cut along its cross section to obtain a freshly exposed surface where phenolphthalein solution was applied. Fresh, unaltered areas of the concrete sample became red or purple, while altered portions remained colorless (Fig. 9). The depth of alteration, defined by the colorless sector of the concrete sample was subsequently measured under the binocular microscope. It ranges from 4 mm to 5 mm within the cement paste which had direct surface contact. For the portion of concrete where aggregates were exposed, deeper alteration levels were measured in the cement matrix ranging from 9 mm to 17 mm.

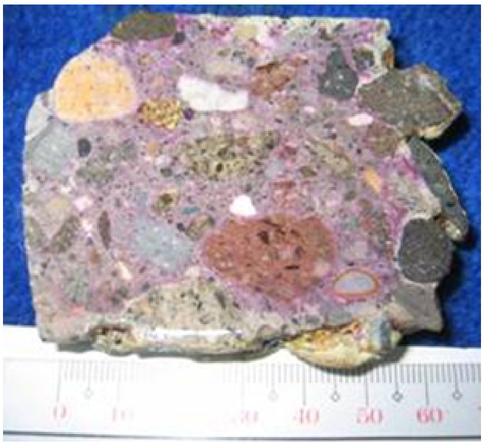

Figure 9: Phenolphthalein Test.

3.2 Petrographic Analysis

Thin sections were prepared for the concrete sample and examined under the petrographic microscope to determine composition of aggregate components, and characterize the matrix and cement paste.

The rounded to sub-rounded aggregates commonly range in size between ~2-4 mm. The aggregate components are mostly volcanic rocks consisting of. porphyritic and non-porphyritic andesitic lavas with variable accessory pyroxene, hornblende, biotite; albitized dacites; hornblende dacites, occasional glass-rich biotite-hornblende tuff, and biotite silicic andesite with secondary quartz. Rare aggregates of medium-grained sandstone and microdiorite are admixed with the dominant volcanic aggregates.

These rock aggregates lie in a primary matrix of cement paste together with smaller, commonly angular fragments (<1 mm) of green-red hornblende, zoned and twinned plagioclase, biotite, andesite, and scoria (Fig. 10). In the outer portion of the concrete sample, the primary cement matrix has been replaced by finely crystalline calcite (Fig. 11). Round vugs are common in the matrix.

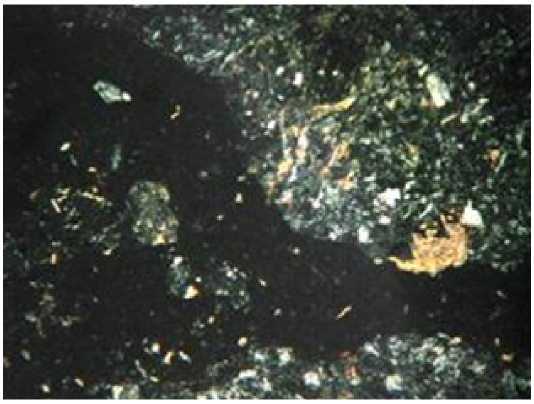

Figure 10: Rock aggregates lie in the original dark cement matrix.

3.3 SEM-EDAX Analysis

The SEM images of the concrete at various magnifications were also taken. The figures at lower magnifications of x50 to x500 (Fig. 12) exhibit the aggregate-matrix texture of the concrete sample. On the other hand, images at higher magnifications of x2000 to x10,000 (Fig. 13) show the secondary calcite crystals and cement paste in the concrete matrix.

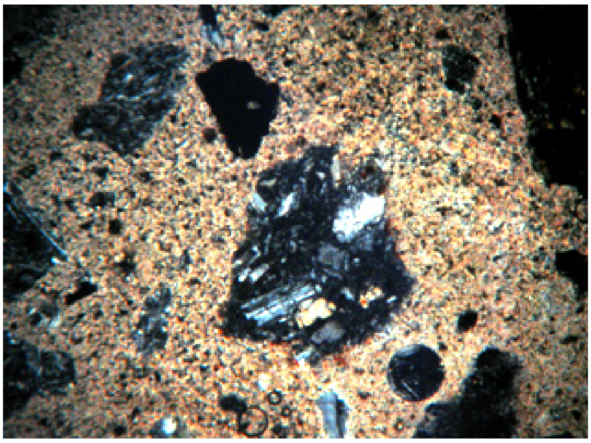

Figure 11: Cement matrix replaced by fine crystalline calcite; round vugs present in the matrix.

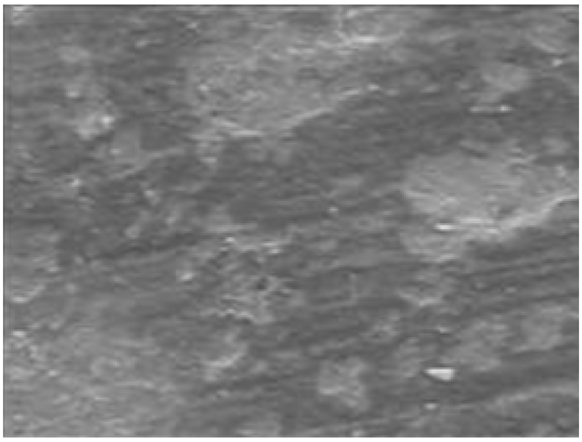

Figure 12: SEM Image of Upper Mahiao ZEDS concrete (x 150)

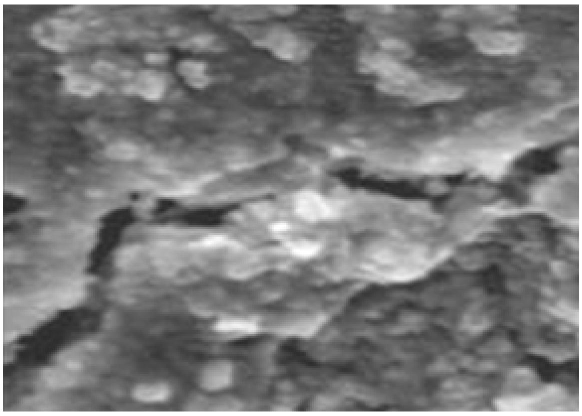

Figure 13: SEM Image of Upper Mahiao ZEDS concrete (x 10,000)

EDAX analysis of cement matrix of the concrete sample (Fig. 14, Table 3) shows the dominance of calcium, carbon, and oxygen confirming that calcite ($CaCO_3$) is the main alteration mineral replacing the concrete matrix as observed in the petrographic examination. Other minor components in the cement matrix are silicon, magnesium, and iron which more likely represent the remaining original cement paste of the concrete.

4. DISCUSSIONS

Based on the results of analyses, the concrete structures of South Sambaloran rock muffler and Upper Mahiao spray tower were both subjected to chemical attack. Sulfuric and carbonic acids coming from power plant effluents reacted with the cement matrix resulting in the formation of anhydrite, gypsum, and calcite in the rock muffler; and calcite in Upper Mahiao. These chemical attacks caused the deterioration of the concrete.

4.1 South Sambaloran Rock Muffler

The deterioration in the South Sambaloran rock muffler is basically attributed to chemical attack promoted by the low pH and the presence of hydrogen sulfide (H_2S). The latter, although a weak acid, may oxidize into the stronger sulfuric acid (H_2SO_4) given the prevailing conditions of high temperature, moisture and oxygen availability. Sulfuric acid is capable of attacking the cement matrix, reacting with the alkaline components, predominantly the $Ca(OH)_2$ resulting from cement hydration to form $CaSO_4$. This explains the concentration of $CaSO_4$ in the vicinity of the exposed surface, as well as the layer of low-alkalinity revealed by phenolphthalein test. The process will be continuous, as the attacked cement matrix is softened and removed by acid, and fresh cement surface is exposed to the aggressive ions. A linear progression with time will give a conservative estimate of the expected progression of concrete deterioration.

4.2 Upper Mahiao ZEDS Spray Tower Posts

The concrete posts of the Upper Mahiao spray tower were subjected to carbonate-rich solutions forming finely crystalline calcium carbonate or calcite ($CaCO_3$) in the cement matrix. Power plant effluents of high CO_2 concentration form carbonic acid in steam condensates which are sprayed onto the concrete posts (Equation 1). Carbonic acid attacks calcium hydroxide in the cement paste converting it to calcium carbonate or calcite (Equation 2) (Erlin and Hime, 2004).

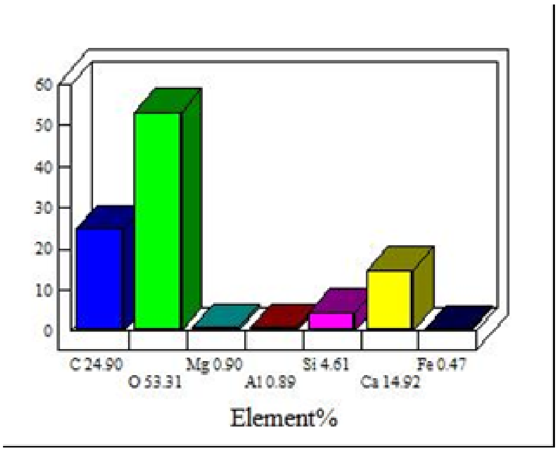

Figure 14: EDX analysis of ZEDS concrete sample.

$$CO_2\,(g) + H_2O\,(aq) \rightarrow H_2CO_3\,(aq) \qquad (1)$$

Dissolved CO_2 in steam condensates forms carbonic acid.

$$Ca\,(OH)_2\,(s) + H_2CO_3\,(aq) \rightarrow CaCO_3\,(s) + 2H_2O(aq) \qquad (2)$$

Calcium hydroxide in cement paste is converted to calcite by carbonic acid.

This carbonation process of concrete will proceed as long as water is present in the system. Hence, calcite formed in the cement matrix can also be later attacked by carbonic acid (Equation 3) resulting in “popcorn-like” calcite crystals, and a highly porous cement paste as observed in the spray tower concrete posts.

$$CaCO_3\,(s) + H_2CO_3\,(aq) \rightarrow Ca(HCO_3)_2\,(aq) \qquad (3)$$

The highly porous cement matrix of the concrete posts became soft and friable; thus, reducing its ability to bind the rock aggregates and making it easily washed away by spraying waters leaving aggregates sticking out of the concrete surface. Based on observations during the PMS, portions of concrete posts being sprayed upon by power plant effluents were most affected by corrosion.

Table 3: EDX analysis of ZEDS concrete sample

Element	Element %	Atomic %
Carbon C	24.90	34.43
Oxygen O	53.31	55.35
Magnesium Mg	0.90	0.62
Aluminum Al	0.89	0.55
Silicon Si	4.61	2.73
Calcium Ca	14.92	6.18
Iron Fe	0.47	0.14
Total	**100.00**	**100.00**

Apart from making the cement matrix porous and friable, carbonation is also undesirable due to lowering of pH of the concrete. Because of its high hydroxide content, fresh concrete has a high pH of ~12 to 13. Upon carbonation, pH of concrete decreases significantly to ~7 which is below passivation threshold of embedded steel in concrete structures (Concrete Experts International, 2006). Hence, carbonation process should be arrested because it may eventually lead to corrosion of reinforcing steel bars in concrete posts.

5. MITIGATING MEASURES

To control chemical attack using the South Sambaloran rock muffler as a case study, the best remedy is to make a dense concrete of low permeability, and to minimize content of chemicals vulnerable to aggressive ions (Torrent, *et al*., 2004). Portlandite content must be kept low and blended cements with high amounts of fly-ash, pozzolan, or blast-furnace slag must be used.

The damaged concrete posts of the Upper Mahiao spray tower were repaired in October-November 2005 during the annual PMS. The spray tower was totally shut down on October 5, 2005, and was drained and cleaned before the start of repair on October 7. The corroded sections of the spray tower concrete posts were removed and resurfaced with a special cement mix of high density blended with fly-ash because it is more resistant to chemical reaction The posts were jacketed up to fluid level, and the tower basin was lined with molded high-density polyethylene plastic that is durable as well as resistant to chemical attack. The rehabilitation of the whole infrastructure was finished on November 15, 2005, and the spray tower was immediately put back in service after completion of the repair.

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formulating remedial measures to arrest further deterioration of concrete structures in the Leyte Geothermal Production Field.

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