Steel Corrosion by Air: South of the Sahara

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Abstract—*Steel is enriched iron (74.5-98.4% Fe) with major metal components and trace elements but its impurities affect the strength. Exposure to an electrolytic air/solution in the atmosphere oxidises the iron component into iron oxides to cause corrosion which speeds up after a long period of exposure at critical pH range of 7.8<pH >5.5. This deterioration may occur uniformly or unevenly when a potential difference is created which may show defects of various textures as pits. Based on the concentration of chlorite, corrosion either commences at the outer or inner rim. Aggressive local corrosion may occur within cracks and crevices. Weathering of rocks could also release into the air and rain, soluble salts which may include sodium chloride. Fine dust which is more severe during the Harmattan over the region south of the Sahara Desert, usually contains sulphide and various salts that could reduce humidity levels. Hence in the Sahel regions, the first rainwater contains also inorganic anions such as NO_3^- and SO_4^{2-} while suspended dust in the air from soil may have elevated levels of Cl^- which promotes corrosion. The rate of electrochemical reactions, diffusion processes and increase in temperature also speed up rate of corrosion.*
Keywords—*Steel, corrosion, iron, Sahara.*

I. INTRODUCTION

To strengthen iron (74.5-98.4%) for production of steel, various elements such as carbon, copper, nickel and manganese are added, while molybdenum and vanadium occur as traces with impurities of silicon, phosphorus, sulphur and nitrogen considered as negative to strength and deformation characteristics [1]. Chemical composition of elements (in %) of an ASTM A36 steel, is C 0.25-0.29, Cu 0.20, Fe 98.0, Mn 1.03, P 0.040, Si 0.28 and S 0.05[2]. The use of this steel include bolts, riveting or welding of bridges, buildings and oil rigs, tanks, bins, bearing plates, fixtures, rings, templates, jigs, sprockets, cams, gears, base plates, forgings, ornamental works, stakes, brackets, automotive and agricultural equipment. The steel is also used for various parts for flame cutting in parking garages, walkways, boat landing ramps, trenches, etc. For plates, ASTM A36 has maximum content of phosphorus and sulphur at 0.03% and is of 380mm width, and thickness >20mm; for bars and plates, the maximum content of phosphorus is 0.04%, sulphur is 0.05%, width ≤380mm, and thickness >20mm.

Despite strengthening and protection against deterioration from weather, all types of steel corrode when exposed to atmospheric conditions. Corrosion begins with exposure to an electrolytic solution which oxidises iron into iron oxides, weaker than steel. Corrosion rate depends upon various parameters, such as period of exposure to moisture, pH of pollutants like sulphates and chlorides of the surrounding environment. Corrosion may occur uniformly or unevenly when a potential difference exists between two different metals immersed in a conductive solution. The deterioration begins as self-catalysed pitting, visualised by the sudden appearance of circular pits with uniform diameters of 6-7μm and depth of about 2-3nm. Such pits are initiated at concentrations above 10mM NaCl, at the outer rim of the confined zone, while below 10mM NaCl, it commences inside the confined zone [3]. Crevice corrosion is a form of local corrosion that may occur within cracks and crevices where depletion and reduced transport of species such as oxygen leads to the development of aggressive local corrosion potentials [4].

Three stages of corrosion in steel are pit growth, crack formation at the pit, and crack propagation [5]. Corrosion of a particular pit size may form a significant risk of cracking in some alloys [6]. Hence corrosion should be treated early before it becomes visible especially in electronics. Pitting corrosion is regarded as one of the most hazardous forms of corrosion for traditional marine and offshore structures as it begins as local accelerated dissolution of metal that weaken structural stiffness and leads to failure in oil leakage, product loss, environmental pollution and loss of life [7]. Severe corrosion regions may tunnel into the matrix of the material beneath the surface, leading to significant complicated damage than simple thinning [8]. Hence it effects mechanical stress and the life span of equipment [9]. In the presence of corrosion, small cracks may grow much faster than large cracks [10]. According to [11] elements in steel like Cl, Cu cause steel to corrode preferentially whereas other metals e.g. Zn, Al, Mg protect steel as they are preferentially more corrosive. Even though substantial savings can be made through the use of corrosion-resistant materials, yet plants could be shut down or

portions of the process stopped because of unexpected corrosion failures.

The rate of corrosion in an environment increases considerably when the relative humidity is 45% or above [12]. There is a linear relationship between the corrosion rate of cast iron and the log of chloride ion concentration, in the pH range 7.8< pH >5.5 [13]. This paper reviewed environmental conditions in West Africa, south of the Sahara Desert and how they promote corrosion of steel.

1.2 Climate of West Africa

West Africa has four broad bioclimatic zones based on latitudinal rainfall gradient from north to south: the Sahel, Sudan, Guinean, and Guineo-Congolian with the lowest rainfall occurring in the Sahel (below 100mm annually) and increasing to the south, with the highest rainfall along the southern coast (up to 5000mm annually). Annual average temperatures are 22-28°C and maximum temperatures can reach more than 40°C in the Sahel in April - September [14]. Countries in the Sahel include Mauritania, Senegal, Mali, Niger, Chad, the Sudan, the northern fringes of Burkina Faso and Nigeria. Near the Gulf of Guinea, precipitation is abundant all year-round; at higher latitudes, precipitation decreases; temperatures in the lowlands are high throughout the year, with annual mean values usually above 18°C with maximum temperatures above 40°C in the Sahel [15]. Moist equatorial air masses originating over the Atlantic Ocean bring annual monsoon rains [16]. Hot, dry continental air masses originating from high pressure system above the Sahara Desert give rise to dusty Harmattan winds over most of West Africa from November to February.

In Ghana, the climate is made up of two seasons. The rainy season lasts from May to September in the north, from April to October in the centre, and from April to November in the south. Along the east coast, the rainy season is shorter and goes from April to June with a break in July and August, and a slight recovery in September and October. The south area has higher rainfall, where precipitation is above 1500 millimeters (60 inches) per year up to 2000mm (80 inches) per year in the small west coast area. In the driest areas at the north, the rainfall amounts to around 1000mm (40 inches) per year, and the eastern coast, which includes Accra, it drops below 800mm (31.5 inches) [17]. Maximum humidity and temperature appears to be uniform at the coastal towns in Ghana, with a drop in the minimum values inland. In the coastal areas, humidity is high throughout the year, in the central and northern parts of West Africa, values below 40% are widespread in January, whereas values over 60% are common in August.

1.3.   Geological Setting

South of the Sahara Desert, occurs the West African craton which consists of the Reguibat shield and the Man shield and made up of Archaean and Palaeoproterozoic granitic rocks. The West African craton is bounded to the north by the Anti-Atlas, to the west by a mobile zone of West Africa, and to the east by the mobile zone of Central Africa (Fig. 1). The West African craton is largely covered by sedimentary rocks of Neoproterozoic and Palaeozoic age, namely, the Tindouf basin in the north and the Taoudeni basin in the central part [18].
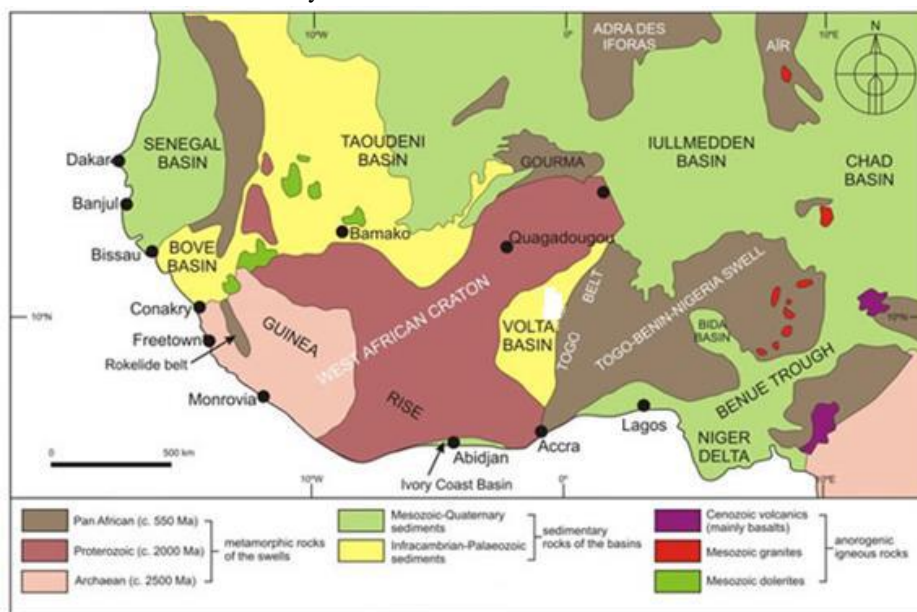

Fig. 1: Geological Map of West Africa showing the Man shield (modified after [21]).

Birimian rocks form a substantial part of the Man shield [18] which occupies the southernmost third of the West African craton. The Man shield comprises a western domain consisting of Archaean rocks of Liberian (ca. 2.75 Ga), Leonian (ca. 2.95 Ga) and pre-Leonian (ca. 3.1 Ga) age [19], and an eastern domain (Baoule-Mossi domain or Birimian/Eburnean province) composed chiefly of Birimian rocks of Palaeoproterozoic age. The Birimian rocks were folded, metamorphosed and invaded by granitoids during the Eburnean event [20]. The Man shield stretches over several countries in West Africa including Burkina Faso, Ghana, Guinea, Liberia, Mali, Niger, Senegal, Sierra Leone and Togo (Fig.1) [21].

In the West African craton, Archean shields and Palaeoproterozoic domains are characterised by iron ore deposits, gold, porphyry copper, lead-zinc, sedimentary manganese ore and primary diamonds that formed also in the Mesozoic; Pan-African and Variscan belts have copper-gold, and Neoproterozoic sedimentary iron ore and phosphate deposits; intra-cratonic and Cenozoic lateritic bauxites, Tertiary/Quaternary mineral sands, oolitic iron ore and sedimentary phosphate deposits [22]. Hence there are many open cast gold mines in West Africa (Fig. 2).
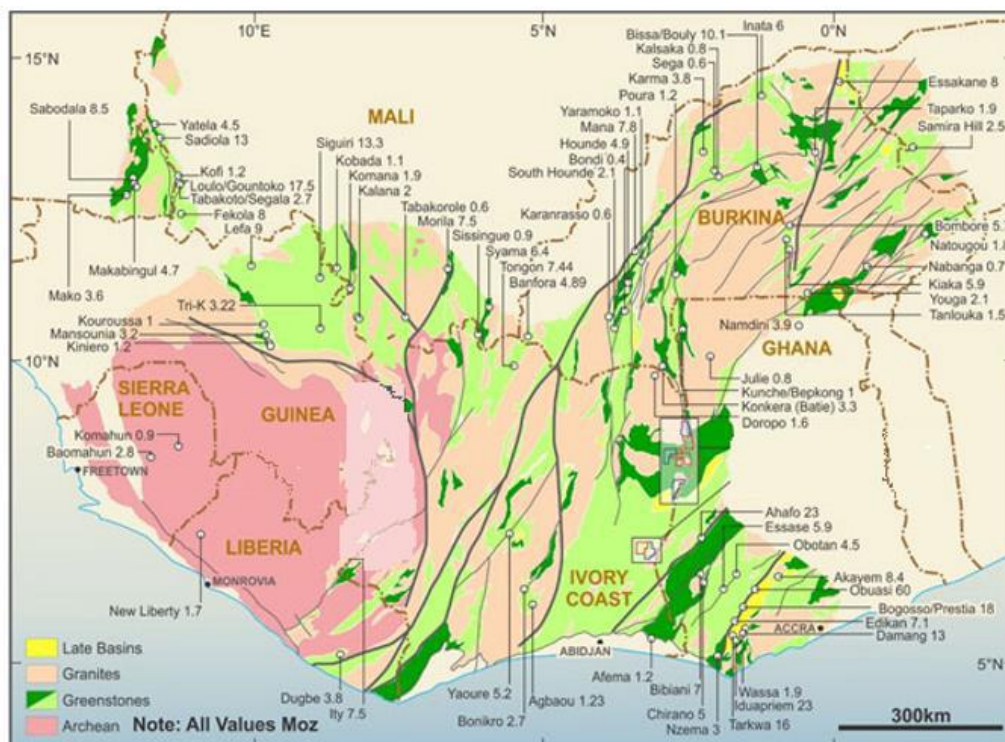

Fig. 2: Geological Map of West Africa showing some major gold deposits.

1.4. Environmental conditions which promote corrosion

About 80% of all deteriorations produced by corrosion in the metallic constructions are due to atmospheric corrosion at rates varying according to geographic zone, season, and atmospheric composition such as pollutants, temperature, humidity, wind speed and direction, etc. [23]. [24], showed the extent of corrosion of electronic materials in aviation as heat (55%), vibration (20%), humidity (19%) and dust (6%). According to [25], there is an average sea surface temperature in the Gulf of Guinea which ranges from 27.13°C for the dry season and 22.52°C for wet season with average sea surface salinity being 35.24‰ and 35.56‰ respectively.

Weathering of rocks produce soluble salts of various types which include chlorides of sodium, calcium and magnesium, sulphates and carbonates. [26], observed that salinity due to accumulated dissolved salts in soil water causes leaching through either natural or human-induced processes leaving sodium bound to the negative charges of clay which can be carried in wind and rain as cyclic salts. Close to the surface, soil water evaporates leaving salts at the soil surface while mobilised salt moves laterally into streams to increase their salinity. The composition of seawater is uniform around the globe. In Lagos, salt content in the air was higher (11.1 mg/dm^3 50m to the surf sea than 1300m away from it (0.2 mg/dm^3) with the rates of rust being 0.95 and 0.4 mm/year respectively [27].

1.5. Intensity of Corrosion Parameters

According to [23], the corrosive effects of chlorite-rich gases and hydrogen chloride in the presence of moisture

tend to be stronger than those of chloride salts because of the acidic character of the gases. [28] showed that pH and temperature also affect microbial activity which contributes to corrosion where the peak can be very acidic or alkaline at maximum pH 9.5 recorded for highest corrosion at highest temperature of 37°C. According to [29], nitrate greatly accelerates the corrosion of iron in acidic solutions, but has slight influence on corrosion in neutral solutions.

[23] showed that deposition of solid matter from the atmosphere can have a significant effect on atmospheric corrosion rates, particularly in the initial stages. Dust usually contains sulphur and various salts that can stimulate atmospheric attack by reduction in the critical humidity levels in hygroscopic action, provision of anions, metal dissolution, and micro-galvanic (preferential corrosion) effects on materials more noble than the corroding metal [30]. According to [31], sulphate levels are not significant at sites north of the equator in Africa. The rainwater in a major mining town in Ghana, Obuasi, according to [32] had a mean pH range from 4.0 to 5.6 which was probably influenced by local mining activities as ionic species are in the order, $SO_4^{2-} > Cl^- > Ca^{2+} > K^+ > Na^+ > NO_3^- = Mg^{2+} > NH_4^+$.

Increase in temperature during constant humidity tends to increase corrosive attack by increasing the rate of reactions and diffusion processes. However, raising temperature, generally, leads to decrease in relative humidity and more rapid evaporation of the surface electrolyte hence relative humidity values higher than 75% and concentrations of pollutants due to presence of SO_2 and H_2S speed up corrosion [24].

II. MEASUREMENT OF SOME ENVIRONMENTAL PARAMETERS IN SELECTED AREAS

According to [33], in the Sahel regions at Banizoumbou, Niger, during June - July 2006, at the beginning of the rains, the total elemental composition of rainwater is dominated by Al, Si, Fe and Ca, and inorganic anions (NO_3^- and SO_4^{2-}) indicating a high influence of dust and limited organic anions of biogenic marine or anthropogenic contribution when vegetation development jumps. [34], analysed rainwater at Tamale in Ghana in 1997 and 1998 during the rainy seasons while road construction was ongoing and observed that there was suspended dust in the air with elevated levels of Cl^- in rainwater higher than the corresponding ratios in seawater. [35], reported that the Sahara desert is a major source of mineral dust on earth as Harmattan dust consists mostly of tiny pieces of metal oxides, quartz, clays and carbonates such as calcite and aragonite, haematite, illite, micas, feldspars, kaolinite and chlorite. [36] also showed that Cu, Fe, Mn and Zn were detected in indoor settled

dust in Makurdi, Nigeria in order of Cu < Mn < Zn < Fe an indication that heavy metals in dust are higher in more industrialised and densely populated cities. According to [37] free-fall rain samples collected at Dzodze in Ghana turned pH of 6.0–6.4, sulphate and nitrate 0.9-3.3 (average 1.77), 0.6-1.0 (average 0.80) mg/l respectively.

[38] harvested rainwater from Uyo municipality of Akwa Ibom State, Nigeria during the rainy season period of April to August and measured pH of 5.90-6.80, nitrate 0.10-0.20 mg/l; Chloride (Cl^-) 22.70-31.20mg/l.

In February, 2015, [39] collected rainwater samples during the time of early rain, when it was expected that there would be more concentration of pollutants in the atmosphere after the Harmattan in Obio/Akpor Local Government Area, Rivers State, Nigeria and recorded pH of 5.71-6.54, sulphate and nitrate 0.09-0.38, 0.0-0.40mg/l respectively; Chloride (Cl^-) 1.31-5.94mg/l.

The pH values of individual precipitation near Obuasi ranged from 4.0 at Wawasi to 5.6 at Antobuasi with a mean value of $4.67 \pm 0.47.SO_4^{2-}$, Cl^-, and NO_3^- made up 84% - high concentration of SO_4^{2-} may be due to the processing of sulphide containing ore accompanied by emission of high amount of SO_2^-[32]. Sulphide gold ores at Obuasi contain arsenopyrite, pyrite and rare pyrrhotite and marchasite [40].

III. CONCLUSIONS

Elements that are usually added to strengthen iron (74.5-98.4% Fe) in steel production are major components and traces with some impurities which affect the strength. Exposure to an electrolytic solution in the atmosphere oxidises iron content into iron oxides to weaken steel during corrosion. This defect speeds up after a long period of exposure to moisture, and pH of pollutants. The deterioration may occur uniformly or unevenly when a potential difference is created in the solution, therefore, showing various defects by appearance of various textures as pits, and based on the concentration of chlorite, either commences at the outer or inner rim. Aggressive local corrosion may occur within cracks and crevices where there is depletion of critical species such as oxygen. It is therefore necessary to identify metal components in steel like Cl and Cu which cause steel to corrode preferentially from metals that protect steel as they are preferentially more corrosive e.g. Zn, Al, Mg.

Weathering of rocks release soluble salts of various types, which may include chlorides of sodium chloride transported also in wind and rain. The fine dust usually contains sulphide and various salts that could reduce the critical humidity levels, the rate of electrochemical reactions, diffusion processes and increase in temperature which lead to a faster rate of corrosion. In the Sahel regions, the first rainwater contains also inorganic anions

(NO_3^- and SO_4^{2-}) washed from dust suspended dust in the air which may have elevated levels of Cl^- that could promote corrosion. Taking into consideration the pH range of 7.8< pH >5.5 critical for the occurrence of corrosion.

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