THE EFFECT OF NITRITE AND CHROMATE INHIBITORS ON CORROSION OF 6063AL IN 0.1M HYDROCHLORIC ACID ENVIRONMENT

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Abstract

This study focuses on the behaviour of aluminium alloy in hydrochloric acid environment where calcium nitrite and sodium chromate are used as inhibitors. Having set up a control experiment of 0.1M HCl, similar acid solution was prepared with various concentrations of the inhibitors. Using a weight loss method, the corrosion of 6063Al alloy samples was measured and the corrosion rates at different concentrations of inhibitors were determined. Performance of each of the inhibitors was assessed and the results obtained compared. It was observed that with increasing inhibitor concentration, efficiency increases. It was also noted that when the concentration of the inhibitors was in excess of 50g/dm^3, the efficiency of sodium chromate is about 4 to 4.5 times more than that of calcium nitrite.

Introduction

Corrosion is the degradation of materials by an electrochemical reaction with its environment. Based on the forms by which it occurs, corrosion can be uniform or general attack, galvanic or two metal corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, selective leaching, erosion corrosion, stress corrosion or combination of any of these (Miksic, 1983, Fontana, 1986 and Lery, 1993).

Corrosion has been a great menace in the work field for engineers and the cost implication is pronounced on the economy of many nations (You et al, 1993). For this reason, research efforts are continually made to check its negative effects on industrial plants, transportation, oil and gas, agricultural and many others. For a given metal or alloy in a given environment, methods adopted to check corrosion include

among others, materials selection, alteration of environment, design, cathodic and anodic protection and coatings (Trethewey and Chamberlain, 1995).

Metallic material exposed to an environment can be ferrous or non-ferrous or their alloys. Aluminium, one of the non-ferrous metals has found wide industrial and domestic applications. It is strongly electropositive and extremely reactive. Therefore, when in contact with air, it rapidly becomes covered with a tough, transparent layer of aluminium oxide that resists further corrosion action (Trethewey and Chamberlain, 1995,). The protective film is generally stable in the PH range of 4.5-8.5, outside this range, aluminium becomes active, its potential becomes more negative and dissolution takes place with the evolution of hydrogen (Rama 1971, Roberge et al, 2002).

Pure aluminium has excellent corrosion resistance, but seldom used in pure form due to its poor mechanical properties. Presence of alloying elements significantly improves its mechanical properties but impairs its corrosion resistance ability (Trethewey and Chamberlain, 1995). The corrosion of Aluminium alloys in any corrosive medium is electrochemical in nature (Draley and Weeks, 1970). The behaviour of aluminium and its alloys when in any corrosive medium depends on the impurities, the alloying elements present, the metallurgical condition and the nature of the dissolved salts. (Robinson, 1979; Klessen et al, 2005).

As a result of its industrial and domestic significance, there have been a number of reports on the corrosion of aluminium and its alloys (Abrahamson et al, 1985, Perkins et al, 1982). Aluminium if introduced into acids exhibit a period of induction due to slow dissolution of the protective alumina (Abrahamson et al, 1985). Cladding with thin sheets of pure aluminium or its alloys and anodising where an electrolytic process is adopted to thicken the surface film to produce a highly adherent layer have proved effective over the years for corrosion prevention of aluminium (Perkins et al, 1982).

Control of corrosion of aluminium has also been accomplished through an alteration of environment, which comprises among others, of application of inhibitors. For proper selection of inhibitors, factors to be considered among others include its concentration, type of environment, temperature and velocity of flow and the type of metallic material exposed to the action of the environment. Such environment can be either

acidic, basic or neutral (Machu 1970; Ebtetial et al, 1998 and Klessen et al, 2005).

Sulphur containing inhibitors have been used to control corrosion of aluminium but have been found hazardous. This is attributed to the formation of M_2S by some of them upon degradation, which promotes hydrogen penetration into metal causing hydrogen embrittlement (Rozenfeild, 1981). Sulphur containing compounds is also found to inhibit corrosion of aluminium alloy in a mixed alloy solution of HCl and H_3PO_4. However the best results are obtained with p-thiocresol and Na-diethyldithiocarbenater (Makwara et al, 1977).

Based on their mechanisms, inhibitors are either anodic or cathodic (Itoh et al, 1990). Anodic inhibitors are either oxidizing or non-oxidizing. Oxidizing inhibitors are those that function at low concentration while non-oxidizing inhibitors are only effective at much higher concentration. Part of their function is to buffer the solution on the alkaline side of neutrality. These inhibitors interfere with the anodic reaction examples of which are sodium phosphate, nitrate and chromate solution (Klyuchnikov et al 1971).

Improper application of some inhibitors can also be dangerous. For instance sodium hydroxide and sodium phosphate, when added in quantity that is just insufficient to abolish corrosion completely localises attack and render it more intense than if no inhibitor had been introduced. This group are almost invariably found among the anodic inhibitors (Burstern et al, 1992 and Shimize et al, 1993).

Prior to its subjection to further treatment such as painting, enamelling, electroplating, cold rolling and others, 6063Al like many metals must exhibit a clean surface free of salt or oxide scales. Hydrochloric acid is the most important pickling acid in use for this purpose due to its economic advantage in the regeneration of depleted pickling solutions. Chromate and nitrite are cheap chemicals that are readily available locally. Though there are many reports on the corrosion of aluminium and its alloys, studies on the control of corrosion of numerous alloys of aluminium are far from being exhaustive. The control of corrosion of 6063Al in hydrochloric acid environment using nitrite and chromate as inhibitors is therefore, the object of this study.

Experimental Procedure

Materials and Specimen Preparation:

The alloy used is 6063Al obtained from Nigeria Extrusion Company Limited (NIGALEX) Lagos. Its composition is presented in Table 1.

Seven rectangular plate specimens of 7cm x 1.9cm x 0.5cm were carefully cut from 6063Al plate and all edges properly smoothened. A hole of 0.45 cm was smoothly punched in each specimen for suspension purpose. To obtain smoothness and cleanliness of surfaces, the each specimen surfaces were ground using fine silicon carbide paper, cleaned and degreased using acetone, air-dried, weighed and stored in desiccators.

Methods

With the aid of sensitive weighing balance, 20g of powdered calcium nitrite [$Ca(NO_2)_2$] and sodium chromate (Na_2CrO_4) were separately measured into beakers and by the addition of distilled water, 20g/dm^3 concentration solution was prepared as inhibitors in each case and their pH values measured. The procedure was repeated to produce concentrations of 70g/dm^3 and 120g/dm^3 for each of the inhibitors and thereafter, 0.1M hydrochloric acid (HCl) was prepared as the corrodant. The ratio by volume of the inhibitor to corrodant is 1:10. Solution of 0.1M HCl was also used as a control experiment.

The specimens were immersed in the prepared solutions and in every 48 hrs, were washed in distilled water, the corrosion product wiped off, dried and weighed. Fresh solutions were prepared after each set of readings. This procedure was repeated daily for 24 days and the readings taken.

Results and Discussion

Results

The results of corrosion of aluminium in 0.1M HCl and the effect of various inhibitors on it are presented in Fig. 1 – 4. The corrosion rate of 6063Al in an uninhibited medium of 0.1M HCl and in solution containing different composition of $Ca(NO_2)_2$ as inhibitors is presented in Fig. 1. Without the use of any inhibitor, the corrosion was very rapid in the first 288 hours, got to peak and started falling gradually. With the use of $Ca(NO_2)_2$, there was an observed decrease in the corrosion rate (Fig.1). The efficiency of $Ca(NO_2)_2$ initially increases and later starts decreasing with time for various concentration (Fig. 2). There was a general decrease in the corrosion rate of 6063Al in HCl when various concentrations of Na_2CrO_4 were used (Fig. 3). Their efficiencies in inhibiting corrosion of 6063Al alloy in HCl

environment is presented in Fig. 4. From the results presented in Figs 2 and 4, their optimum efficiency at various concentrations are obtained and presented in Figs. 5 while their effectiveness at various concentrations are computed from Fig. 5 and presented in Fig. 6.

Discussion

The corrosion rate of 6063Al in an uninhibited medium of 0.1M HCl increases very rapidly from the 48th to 96th hour of immersion. The rate increases progressively until the 288th hour (Fig. 1). The protective oxide surface films (Al_2O_3) on aluminium are readily destroyed by hydrochloric acid (Fontana, 1986). This may be responsible for the observed progressive increase in corrosion rate up to 288th hour. The aluminium alloy is rapidly oxidized (equation 1) by 0.1M HCl (equation 2) resulting to the formation of Aluminium ion and hydrogen gas (equation 3).

$$2Al = 2Al^{3+} + 6e^{-} \quad (1)$$

$$6H^{+} + 6e^{-} = 3H_2 \quad (2)$$

$$2Al + 6H^{+} = 2Al^{3+} + 3H_2 \quad (3)$$

The chemical composition of 6063Al alloy used (Table 1) shows that it contains about 0.3% iron. The presence of metallic ions such as iron and copper tends to accelerate attack (Fontana, 1986). The presence of these metal ions in the solution due to corroded alloy also might have possibly influenced the observed accelerated corrosion rate in the first 288 hours of immersion in the uninhibited HCl solution (Fig. 1).

The corrosion rate remains constant between 288th and 336th hour of immersion after which it starts to decrease (Fig. 1). This may correspond to the period of transition from active to passive behaviour of 6063Al in HCl environment. It is a period of transition from increased chemically reactivity to loss of chemically reactivity experience. There is an observed progressive decrease in the corrosion rate from 336th to the 576th hour. The reason for this behaviour, like some metals and alloys, is probably because when in contact with corrosive medium essentially behave as if they are inert to the environment under certain condition. It is a special case of activation polarization due to the formation of surface film or protective barrier that is stable over a considerable range of oxidizing power (Fontana, 1986).

The corrosion rate in solution containing 20g/dm^3 Ca $(NO_2)_2$ in 0.1M HCl in the first 48 hours of immersion was slightly greater than what was recorded when no inhibitor was added

(Fig. 1). The reason for this may be attributed to nitrite oxidizing aluminium to aluminium ions. Since oxide cannot exist on the aluminium surface in the acidic pH range, this oxidation results in corrosion acceleration (Mustafa and Mhmudal, 1997) which was observed at the initial stage. However, the increase in the rate sharply decreased in the 196th hour and thereafter further decreased very slightly again in the 384th hour before attaining constancy till the 576th hour when the investigation lasted (Fig. 1).

Generally, the corrosion rate declined when $Ca(NO_2)_2$ was introduced into the solution. It was also noted that the extent of decline depends on the concentration of calcium nitrite in the solution. The higher the concentration the lower the corrosion rate with time. Calcium nitrite in the solution of HCl dissociates into calcium and nitrite ions (equation 4).

$$Ca(NO_2)_2 = Ca^{2+} + 2NO_2^- \quad (4)$$

Acidified solution of nitrites is oxidizing agent (Leptrot, 1971). Therefore, nitrite in the solution is oxidized to nitrogen oxide (equation 5) while oxidation of aluminium is suppressed or halted depending on the concentration of NO_2^- in the solution.

$$2H^+ + NO_2^- = H_2O + NO \quad (5)$$

The higher the concentration of the nitrite, the higher the concentration of nitrite ions in the solution and the higher its reduction and consequently, the less the aluminium is oxidized. This could be the possible reason for the observed decrease in the corrosion rate of 6063Al in 0.1M HCl solution when different concentrations of $Ca(NO_2)_2$ were introduced.

Comparing the corrosion rate with the control experiment, as the concentration increases, the inhibitor could be said to be more effective. The higher the concentration of $Ca(NO_2)_2$ in the solution the higher the efficiency attained (Fig. 2). For each of the three concentrations used, the efficiency attains a peak value and starts decreasing.

The efficiencies of solution with 20g/dm^3, 70g/dm^3 and 120g/dm^3 of $Ca(NO_2)_2$ in the HCl acid solution attain a maximum efficiency of 15.30%, 16.00% and 21.40% in the 288th, 288th and 384th hour respectively. Thereafter, the efficiency falls gradually for the remaining part of the test period (Fig. 2). Since the nitrite ions (NO_2^-) in the solution are being oxidized continually with time without being replenished, a time is reached whereby the effectiveness of this inhibitor starts to fall. This could have

possibly explained characteristics of the efficiency of $Ca(NO_2)_2$ exhibited (Fig. 2).

Compared with control experiment, corrosion rate of 6063Al alloy generally reduces drastically with time when various concentrations of Na_2CrO_4 are used as inhibitors (Fig. 3). Unlike the observation with calcium nitrite, the corrosion rate in this case starts decreasing after the first 48^{th} hour of immersion for all the concentration used. Aluminium dissolves into hydrated Al^{3+} ions in acidic medium and Chromate exists as $CrO4^{2-}$ ions also in acidic medium (Liptrot, 1974 and Fontana, 1986). Inhibiting corrosion of 6063Al alloy by chromate in 0.1M concentration of HCl acid may be based on the understanding that, depending on concentration, chromate forms charged complexes or neutral compounds on the Aluminium surface (Mustafa and Mahmudal, 1997). At concentration of 0.1M HCl, neutral aluminium chromate compound formation occurs on the surface of 6963Al which creates barrier against corrosion. Thus, formation of aluminium chromate compounds and its adsorption may be preferred on the oxide free surface (Mustafa and Mahmudal, 1997). This could be the reason for the observed decrease in corrosion rate of 6063Al in 0.1M HCl solution right from the onset when Na_2CrO_4 was used as inhibitor.

It was also noted that the efficiency of the inhibitor also rises with increase in concentration (Fig. 4). The solution with concentration of $120g/dm^3$ proved to be more efficient and attains maximum of 47.70%, 29.80% and 26.30% in an environment containing 70g/dm3 and 20g/dm3 respectively (Fig 4). Higher concentration of Na_2CrO_4 in the solution leads to more availability of the formed aluminium chromate compound and consequently, more efficiency with time. This probably explains why the efficiency increases with increase in concentration.

From the results presented in Figs. 2 and 4, the optimum efficiency of the inhibitors are generated and presented in Fig. 5. Up to concentration of about $50g/dm^3$, the optimum efficiency of each of the inhibitors remains approximately constant. From concentration of $50g/dm^3$ to about $70g/dm^3$, there is about 0.03% and $0.14g/dm^3$ increase in the efficiency of $Ca(NO_2)_2$ and Na_2CrO_4 respectively for every g/dm^3 increase in concentration. This shows that Na_2CrO_4 is about 4.5 times more efficient than $Ca(NO_2)_2$ in this concentration range. Between concentration of $70g/dm^3$ and $120g/dm^3$, the

optimum efficiency of Na_2CrO_4 in solution of 0.1M HCl is about 4 times (400%) more than that of $Ca(NO_2)_2$. This implies that although the optimum efficiency of Na_2CrO_4 in inhibiting corrosion of 6063Al in 0.1M HCl solution is higher than that of $Ca(NO_2)_2$, beyond concentration of $70g/dm^3$, the improvement in the optimum efficiency of $Ca(NO_2)_2$ for every g/dm^3 increase.

To compare the effectiveness of the inhibitors at various concentrations, the increase in efficiency per unit increase in concentration is evaluated (Fig. 6). Increase in efficiency for every unit increase in concentration is the same for solution containing $20g/dm^3$ and $50g/dm^3$. The effectiveness of each of the inhibitors keeps rising as their concentrations increase. It is similarly noted that at same concentration, the effectiveness of Na_2CrO_4 is higher than $Ca(NO_2)_2$ in 0.1M HCl solution (Fig. 6).

Conclusion

The rate of corrosion of 6063Al in an uninhibited 0.1M hydrochloric acid environment is very rapid and it is enhanced by rapid destruction of surface oxide by the acid solution. Generally, the corrosion rate of 6063Al in 0.1M hydrochloric acid environment declines when calcium nitrite or sodium chromate is introduced. The extent of the decline depends on their concentrations.

The observed increase in efficiency of sodium chromate is attributed to the continuous formation and adsorption of aluminium chromate compounds on the surface of 6063Al alloy. The increase in the efficiency also rises as the concentration increases. At the same concentration, the effectiveness of sodium chromate is higher than that of calcium nitrite in 0.1M hydrochloric acid environment.

It is established that the use of sodium chromate and calcium nitrite as inhibitors to the corrosion of 6063Al in 0.1M hydrochloric acid environment is effective; the level of efficiency being a function of their concentration. At a concentration above $50g/dm^3$, the efficiency of sodium chromate is about 400% to 450% the efficiency of calcium in 0.1M hydrochloric acid nitrite.

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Table 1: The chemical composition of the aluminium sample used (NIGALEX, 2002)

Alloy Element	Composition.(%)	Alloy Element	Composition.(%)
Silicon	0.4697	Chromium	0.00987
Iron	0.3224	Titanium	0.0084
Copper	0.0474	Calcium	0.0156
Manganese	0.0331	Selenium	0.002
Magnesium	0.3913	Aluminium	98.663
Zinc	0.0393		

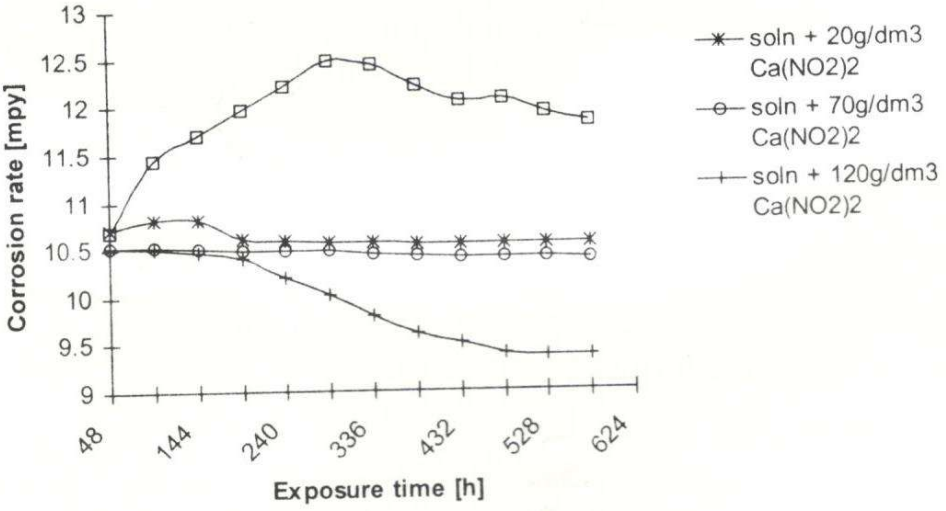

Fig. 1: Corrosion rate of aluminium with time in environment of 0.1M hydrochloric acid containing different concentrations of calcium nitrite

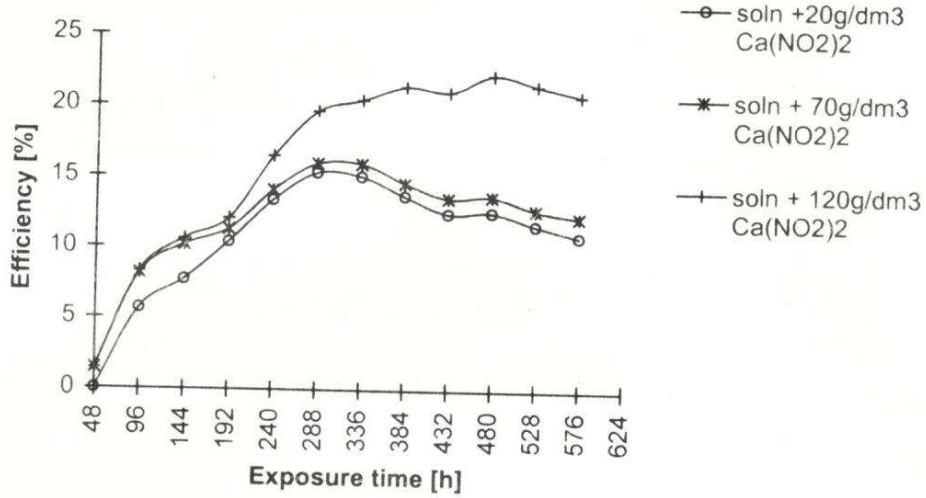

Fig. 2: Inhibiting efficiency of calcium nitrite at various concentrations with time in 0.1M hydrochloric acid environment

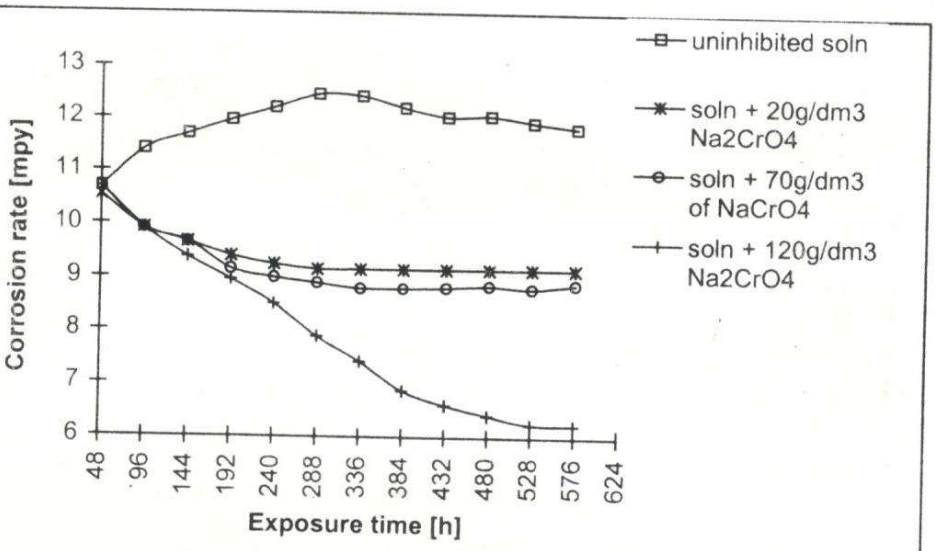

Fig. 3: Corrosion rate of aluminium with time in environment of 0.1M hydrochloric acid containing different concentrations of sodium chromate

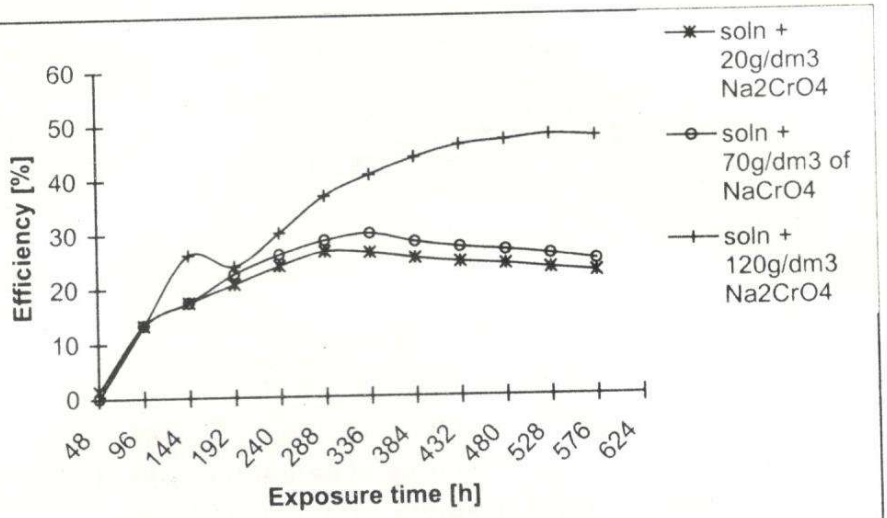

Fig. 4: Inhibiting efficiency of various concentrations of sodium chromate in 0.1M hydrochloric acid environment with time

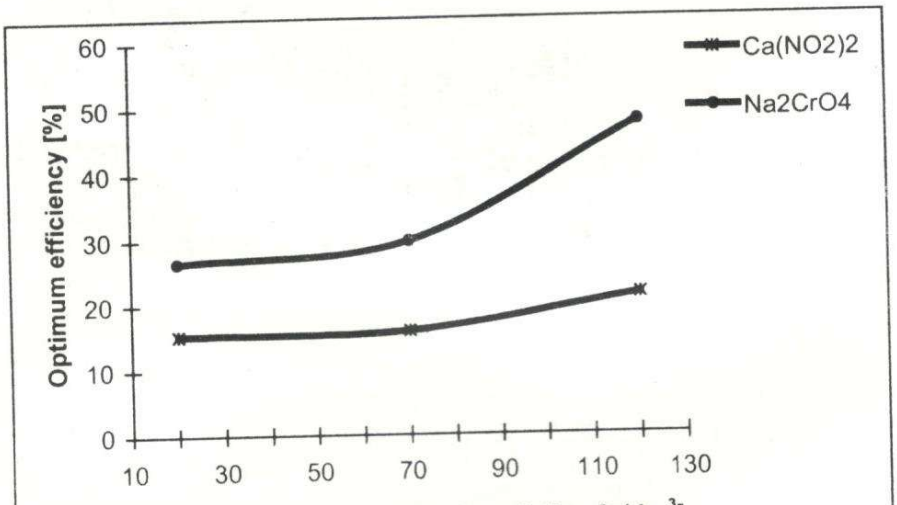

fig. 5: Optimum performance of inhibitor as concentration changes

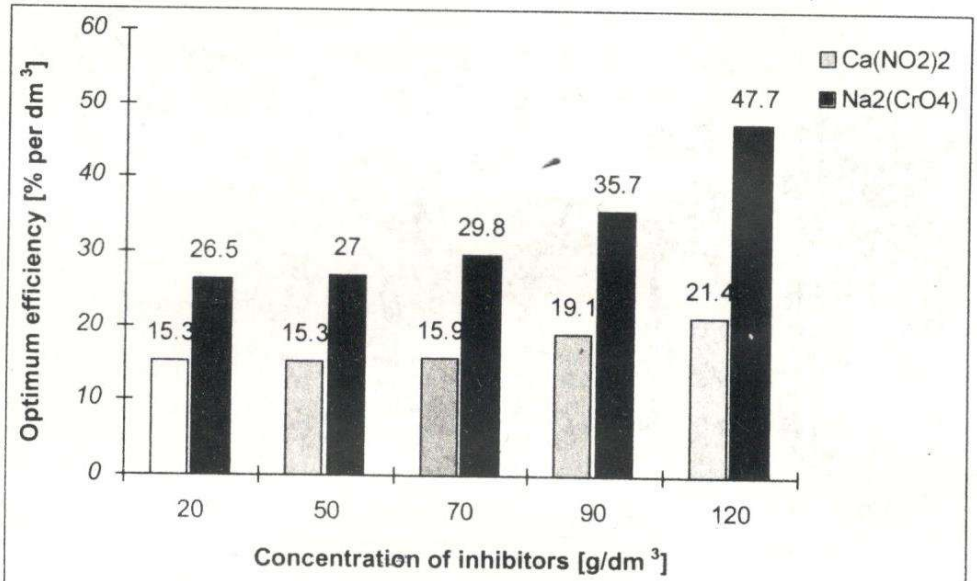

Fig. 6: Effectiveness of inhibitors at dfferent concentrations