

# STUDY of CORROSION CAUSED by CHEMICAL ATTACK of ALKALI SULFATE on MILD STEEL HEAT EXCHANGERS: MODELING and MECANISMES

N. Bensekhri<sup>#1</sup>, H. Essom<sup>#2</sup>

<sup>#</sup> Dept. of Mech. Eng, Skikda University  
BP 26 Route d'El-Hadaiek Skikda 21000 Algeria

<sup>1</sup> nbensekhri@ yahoo.fr

<sup>#</sup> Dept of Metallurgy and Engineering of Materials, Annaba University  
B.P 12, Annaba 23000, Annaba, Algeria

<sup>2</sup> Essom\_h@Yahoo.fr

**Abstract**— The behavior of the mild steel alloy in hot corrosion has been studied in sulphate-chloride atmosphere and in air, examined at 570°C and 650°C in different percent of the mixture for 60 h.

The coated specimens showed an increase of the isothermal oxidation rate. The oxide formed is spalled, cracked and blistered.

A simplified process model based on the chemical kinetics equations of the sulphate –chloride in iron is made. So a mechanism controlled by the complex alkali iron trisulphate formation reaction is proposed. An attempt has been made to evaluate the equilibrium constant and the rate coefficient of the controlling reaction on the basis of the experiment. The model describes quantitatively the rate of steel sample corrosion in molten sulphate at 570°C and 650°C.

The model yields the mass gain profiles as a function of time for particular process conditions and can be used for the evaluation of the coating growth rate and morphology during corrosion.

A principal goal of this study was to identify the role of the molten salt in accelerating hot corrosion.

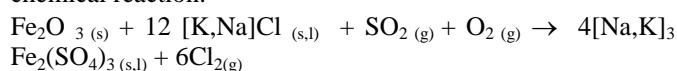
**Keywords**— hot corrosion mechanism, molten salt, modeling, mild steel,

chlorides, these alloys are likely to undergo hot corrosion, even at moderate temperatures compared to their typical maximum application temperature. The presence of molten salt deposits can lead to accelerated oxidation and hot corrosion with the corrosion products comprised of oxides, internal sulfides, and/or internal chlorides. The molten salts will interact with substrat elements ( Fe, Cr, Mn), resulting in sever corrosion causing by oxidation and hot corrosion, both of which have serious effects on the safe of performance of materials.[33]

This accelerated attack results from condensation of films containing molten salts such as sulfates, chlorides, vanadates, carbonates, etc. Particularly, vanadium (V), sodium (Na), and sulfur (S) are the common impurities of low grade petroleum fuel used in oil-fired power stations.

These compounds make low eutectic salts deposits on the materials known as “oil ash”. [9]

Thus the iron oxides react with chloride and sulfur following chemical reaction:



## I. INTRODUCTION

The degradation of the tube of furnace steel due to corrosion is of great concern for the durability of plants structures and implies serious economic losses.

Hot corrosion is a major failure mode for high temperature components of many engineering systems such as aircraft and land-bases gas turbines, fuel oil and coal operated high temperature power generating devices, coal gasifiers, molten carbonates fuel cells, etc .[1–7]

Further studies of the oxidation of heat-resisting steels have been carried out by many authors. [8] In simple oxidation in air, the rate of oxidation becomes very slow at long times.

When the environment in such applications includes condensed molten salts, especially alkali sulfates and alkali

## II. EXPERIMENTAL PROCEDURE

The material investigated was low-alloy ferritic steel. Its composition is given in Table I. The sample pre-treatment procedure was grinding on emery paper, polishing with 5µm diamond paste and degreased in acetone. In order to study the effect of a molten chloride mixture, experiments were carried out with 40% K<sub>2</sub>SO<sub>4</sub> salt mixture in the temperature range of 570: 650 °C. (Figure 1) The detailed procedure of the oxidation tests was explained in the first part of this study [10].

TABLE I  
 CHEMICAL COMPOSITION OF THE STEEL

ELEMENTS	C	Si	Mn	Cr	Mo	S	P
% (BY WEIGHT)	0.015	0.5	0.3	2.6	1.13	0.03	0.03

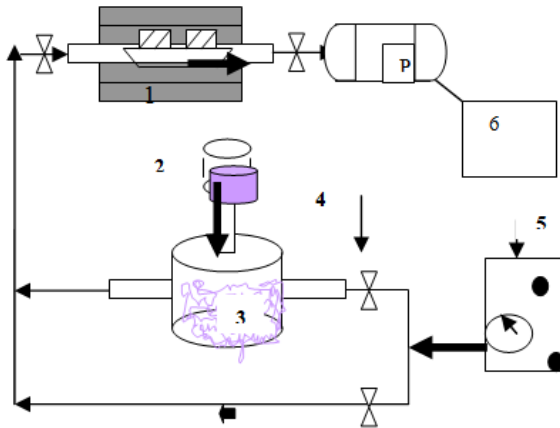


Fig. 1 Schematic representation of the corrosion device in solution mixture ( $K_2SO_4 + NaCl$ ) + air).

- 1- Furnace, 2- Solution ( $K_2SO_4 + NaCl$ ), 3- Fiberglass, 4-valve, 5- Suppressor, 6-vacuum pump.

Some specimens were put in a vitreous silica crucible that contains a salt mixture. Others were oxidized in air. Then we have proceed to do a series of tests to measure the kinetics of oxidation and hot corrosion under air and mixture salt. These tests were carried out in the temperature range of 570–650°C.

Samples were then sectioned to be mounted in evacuated araldite resin for metallographic examination by optical microscopy and scanning electron microscopy (SEM). The remainder was retained for X-ray analysis. Energy dispersive X-ray analysis in the SEM was used to determine the quantity and distribution of elements in the oxide scale.

High temperature corrosion of various amount of deposits (chloride and sulphate) and in air were discussed in our previous paper [10]. We report that the amount of 40 % of  $K_2SO_4$  was retained.

### III. RESULTS AND DISCUSSION

#### III.1 MECANISM OF DEPOSITS FORMATION

One of the main purposes to develop the present model is to estimate the long term behaviors of mild steel in a corrosive molten salt system.

##### III.1.1 FORMATION OF ALKALI CHLORIDE

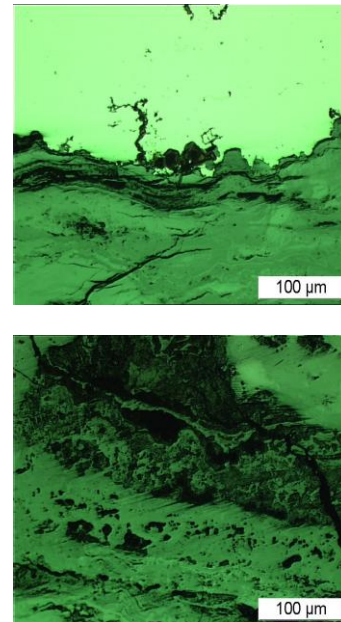
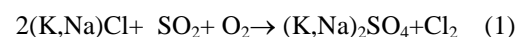


Fig. 2 Microstructure of corrosion section in molten salt (40 %  $K_2SO_4$  + 60% NaCl)

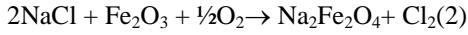
Oxidation can be considerably accelerated in the presence of chlorine, hydrogen chloride and chlorides.

The oxide formed of the coated specimens present cracks and porosities. (figure 2) The origin of gaseous chlorine is attributed to sulfation of alkali chlorides in deposits by  $SO_2$  in flue gases [11, 12, 13, 14], and to reactions between solid chlorides and the oxide scale [12, 15], but also the presence of solid NaCl or KCl in deposits creates an atmosphere rich in gaseous chlorine-containing species.

Chlorine formation occurs from sulfation of chloride-containing deposits according to the reaction:



or from chlorides by reaction with oxides such as Fe<sub>2</sub>O<sub>3</sub>

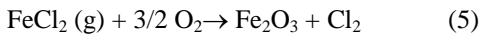
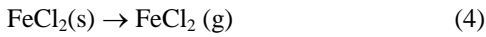


Chlorine can somehow diffuse through oxide scales rapidly and reacts at the interface oxide/metal to chlorides of Fe, Ni and the other alloying elements, e.g.

Cl<sub>2</sub> will penetrate to the surface of metal and react with it:



At high temperatures (500°C) FeCl<sub>2</sub> have a vapor pressure of  $5 \times 10^{-4}$  bar, and will evaporate steadily.



The chlorine from the reaction (5) may enter the atmosphere but mostly it will reenter the scale and continue its catalytic action in the reaction sequence (3), (4) and (5). This process has been described as “active oxidation” in the literature. So when the Cl<sub>2</sub> reenters the scale, the active oxidation is a circuit catalyzed by chlorine, leading to an unprotective oxide scale. The circulation of chlorine in oxidizing and reducing atmosphere is modeled in Figure 3.

According to thermodynamics metal chlorides, the FeCl<sub>2</sub> (g) passes through cracks and pores of the scale outwards, and when reaching regions with sufficient oxygen pressure it is oxidized. Then layers of Fe<sub>2</sub>O<sub>3</sub>, result from the evaporation and oxidation of FeCl<sub>2</sub>, oxide bubbles arise where such layers are cracking and repeated spalling and cracking leads to a multilayered scale [9].

Scale removal effect makes the high temperature oxidation in liquid metal flow environments very complicated, together with the selective corrosion and/or oxidation caused by the alloy components and metallurgical impurities [7].

The corrosion was more severe than in tests performed in the same atmospheres without salt deposits, reported in a previous paper [10].

According to Grabke et al. [16] the partial pressure of Cl<sub>2</sub> below chloride containing deposits is in the range of 10<sup>-10</sup> - 10<sup>-13</sup> bar. In oxidizing combustion atmospheres metal oxides are stable, even if gaseous chlorine is present. However, the partial pressure of oxygen below the oxide layer is low, corresponding to the partial pressure needed for oxide formation.

It is noticed by several researches [17][18][19][20] that the effect of the sodium chloride NaCl is the formation of the eutectic (with low welding point) with Na<sub>2</sub>SO<sub>4</sub> and the

After studying the effect of chloride, we suppose that the effect of chloride has the role of cracking and create the removal scale to allow easy access to sulphates in the scale, so suppose that the reaction of complex sulphates formation control the process of corrosion.

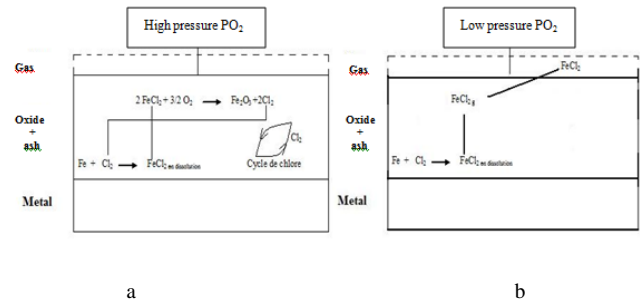


Fig. 3 Model for salt melt induced of Fe showing the reaction mechanism (circulation of chlorine in active oxidation process).  
 a- oxidizing atmosphere  
 b- reducing atmosphere

### III.1.2 FORMATION OF ALKALI SULFATES

After the study of the behavior of the chloride on steel, it was of fundamental interest how the sulphates behave in the corrosion process.

It has been reported [25] that, as the temperature increases in the range 500-750°C, the alkali iron trisulphate melts at 565°C and then resolidifies at 700°C.

#### III.1.2.1 MECHANISM OF SIMPLE CHEMICAL REACTION

The presence of the melt sulfate on the surface of steel leads to increasing of the corrosion by dissolution of the passivate layer (the oxide). [26]

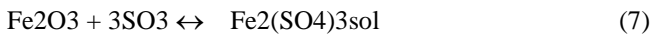
The rate of O<sub>2</sub> diffusion is larger than that of SO<sub>3</sub>, so then at the sample surface there is always sufficient concentration of O<sub>2</sub> to form steady layer of Fe<sub>2</sub>O<sub>3</sub>. Corrosion occurs as a result of dissolution in the molten sulphate at the scale–melt interface [25]

Previous research in this field reported in the literature states, that if pyrosulfates are formed, then the liquid phase may have a melting point as low as 400°C. [27]

The formation of sulphur trioxide can be obtained, in atmosphere containing O<sub>2</sub> and SO<sub>2</sub> at 600°C, by the following reaction:



Oxygen and sulphur trioxide diffuse through the layer of the molten sulphates deposit towards the steel sample, where they are consumed on the surface.



The equilibrium constant can be calculated according to:

$$k_p = \frac{a_{\text{Fe}_2(\text{SO}_4)_3}}{a_{\text{Fe}_2\text{O}_3} a^3_{\text{SO}_3}} \quad (8)$$

K<sub>p</sub> : the equilibrium constant

The attack occurs through different stages: first a liquid Fe<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>SO<sub>4</sub> phase is probably formed from the initially pure solid Na<sub>2</sub>SO<sub>4</sub> layer; then accelerated oxidation goes on by SO<sub>3</sub> inward diffusion and iron outward diffusion through the molten salt.

At the beginning, the oxidizing species in the gas phase (mainly O<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub>) diffuse through the solid salt layer and reach the metal surface where the formation of a solid scale takes place. At the same time, the formation of FeSO<sub>4</sub> in solution with Na<sub>2</sub>SO<sub>4</sub> occurs according to the mechanism previously discussed. The salt mixture, which is initially solid, becomes liquid when the iron sulphate concentration reaches a critical value corresponding to the phase transition. The melting process could be quite rapid, lasting only a few minutes, as the kinetic curves never exhibit an induction period. Once the salt layer is completely liquid, SO<sub>3</sub> migrates inwards from the gas-salt interface as a consequence of equilibrium, and can react at the salt-scale interface to form oxide and/or sulphate: [28]

Under local equilibrium conditions at the salt/scale interface, the liquid salt cannot be in direct contact with the pure metal. Transport of sulphur trioxide through the deposit

Oxygen and sulphur trioxide diffuse through the layer of the molten sulfates deposit towards the steel sample, where they are consumed on the surface. The presence of any catalyst within the melt (even Fe<sub>2</sub>O<sub>3</sub>) can enhance trioxide formation. (Figure 4)

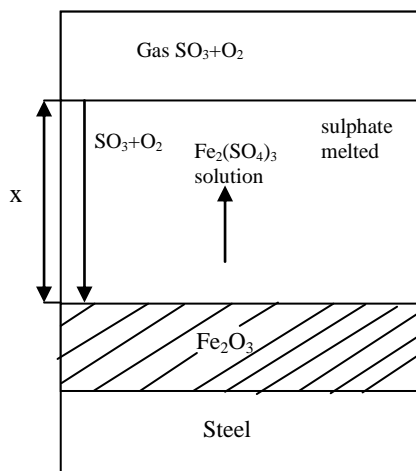


Fig. 4. Schematic description of the material oxidation in molten sulphate.

Assuming a molecular diffusion of SO<sub>3</sub> through a one dimensional layer of molten sulphates, we can calculate the surface density flux of SO<sub>3</sub> [29]:

$$n_{\text{SO}_3} = D_{\text{SO}_3} C_m \frac{a_{\text{SO}_3}(\text{liquide, gaz}) - a_{\text{SO}_3}(\text{liquide, Fe}_2\text{O}_3)}{X}, \text{mol} / \text{m}^2 \cdot \text{s} \quad (9)$$

D<sub>SO<sub>3</sub></sub>: diffusion coefficient of SO<sub>3</sub> through the molten sulphate

C<sub>m</sub>: concentration of the molten sulphate

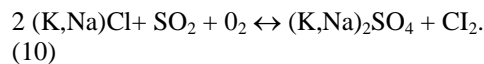
X: molten layer height

a<sub>SO<sub>3</sub></sub>: activity of SO<sub>3</sub> in the molten sulphate.

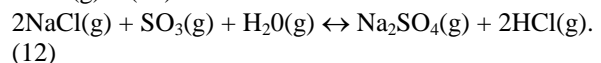
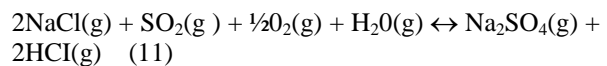
### III.1.2.2.1 Mechanism of complex reactions

#### III.1.2.2.1 Formation of Na<sub>2</sub>SO<sub>4</sub>

The conversion of chlorides into sulphates is given following the reaction:

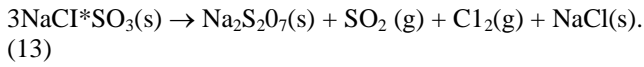


Typical examples are the failures of superheaters and reheaters in oil- and coil-fired boilers due to the accumulation of alkaline and alkaline-earth mixtures of molten sulphates on the surface of ferritic or austenitic steel tubes, through which steam flows. Coal and oil contain sodium impurities in the form of aluminosilicates and NaCl; the latter vaporizes at the flame temperature. Sulphur oxides that are formed from fuel sulphur impurities during the combustion process, can react with NaCl and water to form sodium sulphate[28]:

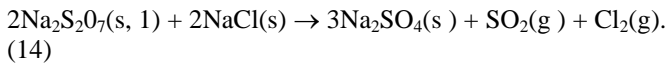


A full description of the process should also consider the equilibria involving Na (g) NaO (g) and NaOH(g), which are species present in the combustion flames. The deposit formation occurs by salt condensation and accumulation if the temperature of the collecting surface is below the sodium sulphate dew point, which is a function of the operating conditions. [28]

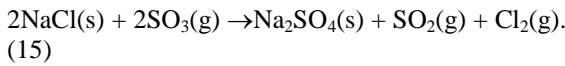
The formation of pyrosulfates has been proposed by several authors, but only in a few cases with analytical proof have been reported. Hixson and Tenney [30] have examined the formation of pyrosulfates and suggest that sodium pyrosulfate is formed from a charge transfer compound NaCl\* SO<sub>3</sub>. This compound is formed from sodium chloride and sulfur trioxide and is stable between 115 and 225°C. Between 225 and 300°C the charge transfer compound undergoes a reaction in which sodium pyrosulfate is formed: [31]



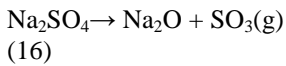
Above 330°C sodium pyrosulfate and sodium chlorides react to give sodium sulfate, sulfur dioxide and chlorine:



The overall reaction above 330°C is then:



Another important characteristic of the molten salts was its character acid-basic, where the  $\text{SO}_3(\text{g})$  it is the sour component in the sulphates. These characteristics based on the concept of Lewis and Lux–Flood that speak of the ability of oxide to donate load or to accept it electronically, consider that, for example for the molten  $\text{Na}_2\text{SO}_4$ , it has the following balance:



the activity parameters and partial pressure are:

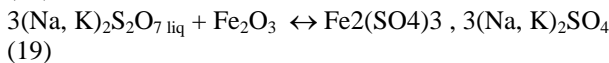
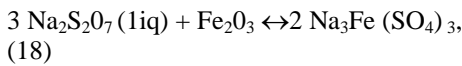
$$\log a_{\text{Na}_2\text{O}} + \log P_{\text{SO}_3} = \Delta G^{\circ}_2 / 2.303RT = -16.7 \text{ at } 927^{\circ}\text{C} \quad (17)$$

where the parameter  $-\log a_{\text{Na}_2\text{O}}$  can be taken as a measure of the salt basicity. In accordance with the previous expressions it is obvious to consider to (basicity) and  $\log P_{\text{SO}_3}$  (acidity) for  $\text{Na}_2\text{SO}_4$ , besides the partial pressure of the  $\text{SO}_3$  in balance with  $\text{Na}_2\text{SO}_4$  fixed the activity of  $\text{Na}_2\text{O}$  or the melting basicity [32]

### III.1.2.2.2 Formation of pyrosulphate

The metallic sulfates [ $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{NiSO}_4$ ] react with ashes such as  $\text{Na}_2\text{SO}_4$  to form a eutectic at temperatures met in the condensed layers.

The Na- K-pyrosulfates are liquid at reaction temperature (500°C). If the melt of them reaches the scale, it will be converted to a complex sulfate :



Such reaction lead certainly to destroy the oxide scale, the overall mass gain of the reactions (10) and (11) is increasing, however, an unprotective scale is formed, and consequently the oxidation of the metal is significantly accelerated.

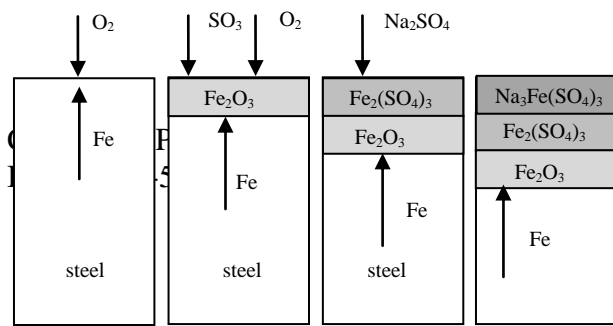
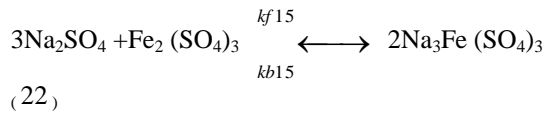
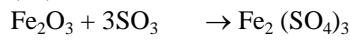
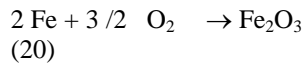


Fig 5. Schematic representation of the effect of molten sulphate processes in heat exchangers in molten salts deposits

This schematic representation for sodium sulfate, sulphur dioxide molecular transport through the oxide scale can be developed from consideration of the following reactions (figure5):



### III.3 Chemical kinetic model (rate equation)

Analysis of kinetic behaviour caused by a parabolic rate of weight gain of weight loss that occur at the same time is often carried out using the chemical kinetic equation, devised for growth of the oxide layer, with accompanying loss of iron from the outer surface of the scale.

Hendry and Lees [25] established that within the nominal mass content 15–50% of  $\text{Fe}_2(\text{SO}_4)_3$  the basic phase in the sulphates system is  $(\text{Na},\text{K})_3\text{Fe}(\text{SO}_4)_3$ , this phase this phase is a complex sulphate most probably are formed in reaction (22).

The expression of the flux is given by:

$$J = \frac{dn}{dt} = V \cdot n_m$$

Where

$n_m$ : number of moles of the molten phase

$V$ : speed

The concentration (in mole / liter) can be calculated depending on the relation:

$$C = \frac{n}{v} \quad (24)$$

$n$ : number of mole

$v$ : volume

At the equilibrium,  $Kp_{15}$  is defined as:

$$Kp_{15} = \frac{k_{f15}}{k_{b15}} \quad (25)$$

Where:

$k_{f15}$  : rate coefficients of reaction (22) in the forward direction

$k_{b15}$  : rate coefficients of reaction (22) in the backward directions

Assuming that corrosion is controlled by reaction (22), we can write a kinetic equation:

$$\frac{dn_{Na_3Fe(SO_4)_3}}{dt} = n_m k_{f15} \left[ a^3_{Na_2SO_4} \cdot a_{Fe_2(SO_4)_3} - \frac{a^2_{Na_3Fe(SO_4)_3}}{Kp_{15}} \right] \quad (26)$$

Applying then numerical integration of differential equation (26), we can have the following expression:

$$\left[ Na_3Fe(SO_4)_3 \right] = \sqrt{Kp_{15}} \sqrt{a^3_{Na_2SO_4} \cdot a_{Fe_2(SO_4)_3}} \frac{e^{\frac{2\sqrt{Kp_{15}} \cdot a^3_{Na_2SO_4} \cdot a_{Fe_2(SO_4)_3}}{v} At}} - 1}{e^{\frac{2\sqrt{Kp_{15}} \cdot a^3_{Na_2SO_4} \cdot a_{Fe_2(SO_4)_3}}{v} At}} + 1} \quad (27)$$

The well-known relation (n=m/M) can be used to estimate the oxide growth approximately. If we use this relation, the equation 27 can be rewritten in terms of weight gain:

$$\frac{\Delta m}{s} = M \times \delta \times \sqrt{Kp_{15}} \sqrt{a^3_{Na_2SO_4} \cdot a_{Fe_2(SO_4)_3}} \frac{e^{\frac{2\sqrt{Kp_{15}} \cdot a^3_{Na_2SO_4} \cdot a_{Fe_2(SO_4)_3}}{v} At}} - 1}{e^{\frac{2\sqrt{Kp_{15}} \cdot a^3_{Na_2SO_4} \cdot a_{Fe_2(SO_4)_3}}{v} At}} + 1} \quad (28)$$

A is the product of  $n_m k_{f15}$ .

M: molar masse of  $Na_3Fe(SO_4)_3$

$n_m$ : number of moles of the molten phase.

Other parameters such as the thickness  $\delta$  are reported in the table (Table- 1).

The following activities are given by the reference [25]:

$$a_{Fe_2(SO_4)_3} = 3,4 \times 10^{-11}; a_{Na_3Fe(SO_4)_3} = 0,132; a_{Na_2SO_4} = 0,413; a_{Na_2SO_4} = 0,454; a_{Fe_2O_3} = \text{traces.}$$

Consequently we are able to calculate the proximate value of the equilibrium constant of reaction 22:

$$Kp_{15} = \frac{a^2_{Na_3Fe(SO_4)_3}}{a^3_{Na_2SO_4} \times a_{Fe_2(SO_4)_3}} = 7,3 \times 10^9. \quad (30)$$

TABLE 2. MATHEMATICAL MODEL DEDUCED FROM THE CALCULATED

NUMBER OF CURVE	OXIDATION CONDITIONS TEMPERATURE/ MILIEU	THICKNESS MEASURED OF THE OXIDE LAYERS (CM)	CALCULATED $K_F$	MATHEMATICAL RELATIONSHIP
1	650 °C/ SALT MIXTURE( $K_2SO_4$ , $NaCl$ )	0.24	0.197	$Y1=13.08 \cdot (EXP(.0689 \cdot X)-1) / (EXP(.0689 \cdot X)+1)$
2	650° C/AIR	0.20	0.149	$Y2=10.90 \cdot (EXP(.064 \cdot X)-1) / (EXP(.064 \cdot X)+1);$
3	570° C/ SALT MIXTURE( $K_2SO_4$ , $NaCl$ )	0.066	0.062	$Y3=3.6 \cdot (EXP(.08 \cdot X)-1) / (EXP(.08 \cdot X)+1);$
4	570 °C/AIR	0.060	0.056	$Y4=3.32 \cdot (EXP(.08 \cdot X)-1) / (EXP(.08 \cdot X)+1);$

PARAMETER ACCORDING TO THE EXPERIMENTAL RESULTS

### III VALIDATION

It is interesting to test the models by comparing the form of the curves obtained using the values of the model according to equation 28 with the experimental recorded data for weight gain show the recorded data and four curves constructed using various values for the rate constants from Table 2. There is good agreement between simulated and experimented weight gains curves and show an almost parabolic relationship between weight gains and time (figure 6).

It is important to notice that this model is based on a lot of suppositions for the lack of certain experimental data.



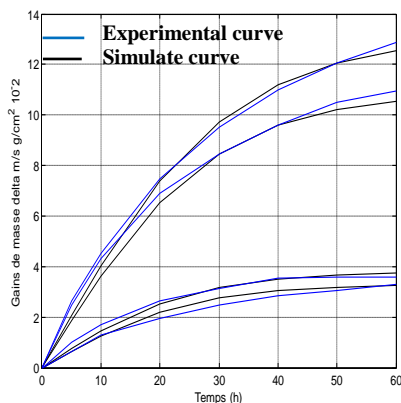


Fig 6 Comparison of experimental and simulate curves.

It is important to notice that this model is based on a lot of suppositions for the lack of certain experimental data.

#### IV CONCLUSIONS

The present investigation aimed at understanding the mechanism of corrosion of the iron-based alloy. In order to describe the kinetic behavior of iron in these environments, curves issued by the mathematical equation need to be compared to the experimental data and include terms for scale growth.

From these results, next conclusions can be withdrawn:

- 1-The presented mechanism, based on the assumption that reactions of complex sulphates formation control the process, enables the calculation of the rate of steel corrosion in a molten deposit.

Calculations based of the model equation show that developed model is benchmarked with experimental data, and good agreement is obtained. It is concluded experimentally that the weight change has confirmed the effect of the melting point of alkali metal sulphate deposits typical of those found on exchangertubes in the corrosion rate. Small amounts of  $Fe_2(SO_4)$  have a significant effect and decrease the melting point of the minimum liquidus composition of  $Na_2SO_4-K_2SO_4$  mixtures from 820°C to 550°C[ ]. There is a range of composition in which the melting point of Na-K-Fe

trisulphate is below the normal range of exchanger operating temperature.

This process has been demonstrated experimentally

3-The mechanism of corrosion of alloy by molten sulphates and the observed temperature dependence can be related to the melting point behavior of the sulphates.

4-A model based on hot corrosion of salt mixture successfully predicts the observed behavior of mild steels in service under conditions of molten sulphate attack.

The influence of certain compounds such as composition of steel on the corrosion rate still is an open question and it can be solved by application of the activation coefficients for most important deposit components. This difficult problem demands additional experiments.

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