



# Monitoring of 13% Cr martensitic stainless steel corrosion in chloride solution in presence of thiosulphate by acoustic emission technique



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## ABSTRACT

Corrosion behaviour under tensile load of 13% Cr martensitic stainless steel in an acidified chloride solution in presence of thiosulphate ions ( $10^{-2}$  M) was evaluated by acoustic emission (AE) technique. AE source localization along specimen length allowed to identify different damage mechanisms characterized by specific AE parameters. Few large pits have been observed on specimen surface. Pit growth mechanism changed during time. All specimens failed after about 300–400 h by cracks originated at a pit tip. Cracks started to propagate in a cleavage microductile mode and then propagate in a brittle intergranular mode. Final rupture was characterized by ductile propagation.

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## 1. Introduction

Corrosion is one of the main concerns in Oil & Gas industry [1,2]. The increasing demand in oil and gas production pushes toward the exploitation of deeper wells and as a consequence to face with more and more aggressive environment. This requires the use of ever more corrosion resistant alloys [3] and to push such alloys and low alloy steels to their limits [4,5]. For this reason the interest on martensitic and supermartensitic stainless steels for application in oil and gas industry is continuously growing due to their good corrosion resistance and mechanical properties as a valuable cost effective alternative to duplex stainless steel for high CO<sub>2</sub>, medium to high chlorides and low H<sub>2</sub>S content environments [4,6,7]. Hydrogen sulphide (H<sub>2</sub>S) is the more relevant constituent of sour gas environment, since its high aggressiveness and to avoid costly equipment faults, to minimize the health and safety risk to the public, personnel and to the environment, specific attention was given by the international scientific community to the identification of the application limits of metal alloys [8]. Brine saturated with H<sub>2</sub>S have been used traditionally to investigate the sour gas resistance of materials as recommended by NACE Standard TM-177 [9]. On the other hand H<sub>2</sub>S is identified as one of the most toxic, flammable and corrosive substances [10–12], rais-

ing several problems in testing laboratory due to safety limitation and to the expensive equipments and confinement devices needed. Starting from the proposal of a Japan research group [13] several authors suggested the use of brine containing thiosulphate solution to simulate the sour gas environment [14–17]. Actually corrosion in thiosulphate solution in presence or without chloride is a well known and deeply studied problem. Corrosion failures as a consequence of intergranular stress corrosion cracking (IGSCC) induced by thiosulphate ions were observed in the pulp and paper industry [18–20]. Also, thiosulphate ions have been responsible of several failures in the nuclear industry [21–25]. The role of thiosulphate on localized corrosion of stainless steel was extensively studied since the 80's [20,26–30]. A critical review on the role of thiosulphate in the corrosion of steel has been recently published by Choudhary et al. [31], while corrosion mechanisms in sulphur-water systems have been deeply analysed by MacDonald [32] and Schmitt [33].

Garner [34] and Newman [26,35] studied the thiosulphate induced corrosion on stainless steel in chloride containing environments. They concluded that at high concentration thiosulphate has an inhibiting effect on pit propagation due to preferential electromigration of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> into pit nuclei, so preventing chloride accumulation and probably retarding acidification. At low concentration not enough thiosulphate can reach pit nucleus so inhibiting pit propagation. It was further reported that the thiosulphate pitting occurred not only in the narrow range of ionic concentration, but also over a limited range of potential. If the potential is too oxidizing, the absorbed sulphur species cannot be generated and

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alloy behaves as though thiosulphate was absent, consequently pitting corrosion can occur only if chloride ion concentration is sufficiently high. The effect of potential on the corrosion in thiosulphate solution was explained on the basis of E-pH diagrams for sulphur species on Fe, Ni and Cr by Marcus and Protopopoff [27].

The most commonly-advanced mechanism of pitting by thiosulphate is based on the reduction of thiosulphate to the adsorbed sulphur, which inhibits the repassivation process once pitting is initiated [29,32]. It was further hypothesized that thiosulphate alone has no aggressive effect on the passive film, and only aggravates pitting on the bare metal surface once the chloride has induced film breakdown (although quantitative confirmation of this speculation was not performed) [35]. More than absolute thiosulphate concentration the ratio  $[Cl^-] + [SO_4^{2-}]$  to  $[S_2O_3^{2-}]$  was judged fundamental, a ratio between 10–30 was considered most aggressive [26]. At the same chloride to thiosulphate ratio, by changing the ions concentration a change in pits morphology was observed [28].

As already mentioned thiosulphate ions was also responsible for intergranular stress corrosion cracking (IGSCC) of stainless steel alloys [36–40]. Cracking of sensitized Type 304 SS steel is electrochemically controlled and SCC was found not to occur at potentials less than  $-0.5$  V(SCE) [36]. The maintenance of an acidic environment at the crack tip seems to be a necessary condition for SCC, and a decrease in pH was shown to increase the crack nucleation rate [40]. It was supposed that during cracking the metastable sulphur anions,  $S_2O_3^{2-}$  are readily converted to elemental sulphur at the advancing crack tip surface, which retards the repassivation and increases anodic dissolution as well as inhibiting recombination of hydrogen atoms on the surface [31].

SCC of non sensitized steels have been also reported in the chloride containing thiosulphate solution [13] and evidenced by slow strain rate tests [37,41]. The influence of thiosulphate concentration as well as of solution pH on SCC of martensitic steel was evaluated by Zucchi and co-workers [14], no SCC was observed at low thiosulphate concentration below  $10^{-5}$  to  $10^{-6}$  M (depending on the alloys) and pH above 4.5. In a more recent study, the SCC behaviour of low nickel grade duplex stainless steel (LDX 2101) was studied by Zanotto and co-workers using the SSRT technique [17]. A susceptibility to SCC in 20% NaCl solution at  $80^\circ\text{C}$  in the presence of thiosulphate was evidenced for the LDX 2101 alloy, the highest susceptibility to SCC was observed for  $10^{-3}$  M thiosulphate solution. At higher concentrations of thiosulphate, the selective corrosion of ferrite became competitive with SCC, which only led to generalized selective attack of ferrite phase, thus reducing the SCC susceptibility.

The advantages in using Acoustic Emission technique (AE) to study SCC [42–47] and pitting [48–50] have been clearly evidenced in literature. AE technique was in particular used to evaluate initiation and propagation steps in pitting corrosion of austenitic stainless steels [48,49]. In the early stage of pitting initiation acoustic emission events have not been related to the corrosion process itself but to the more acoustical active mechanism of hydrogen evolution [50] mainly as a consequence of bubbles friction along pit walls [48,51]. Either short range mechanic crack propagation (due to high stress intensity at nucleated SCC crack tip) [52] and long range propagation mechanism (assisted by anodic dissolution at the crack tip) [53] have been successfully identified by AE technique. In the former case the crack propagation was associated to high amplitude AE hits (in the range 50–70 dB) while lower amplitude hits (in the range of 40–50 dB) have been associated to the latter mechanism.

Aim of the present work is to study the evolution of the different mechanisms involved in the corrosion of a 13% Cr martensitic stainless steel in chloride solution in presence of thiosulphate at constant chloride to thiosulphate molar ratio by means of AE technique. A fixed thiosulphate ion concentration was used in this

**Table 1**  
X12Cr13 martensitic stainless steel chemical composition.

Composition [wt%]							
Fe	C	Mn	Si	P	S	Cr	Ni
balance	0.13	0.43	0.29	0.020	0.001	12.18	0.21

work and only preliminary results based on univariate and bivariate analysis are here reported. The evaluation of the influence of thiosulphate concentration on failure mechanisms and the use of a more sophisticated cluster analysis of AE data based on the use of self organizing maps algorithms is still under development and will be reported in a further publication.

## 2. Experimental part

### 2.1. Materials

Specimens for corrosion tests were made of X12Cr13 (UNS S41000) martensitic stainless steel whose composition is reported in Table 1.

Tensile specimens were made in accordance to NACE TM077 method A [9]. Gauge section had a diameter of 3.81 mm and a length of 15 mm. Specimens were machined from a forging disk. In detail, specimens were extracted along the circumferential direction at maximum diameter in order to get higher mechanical properties and toughness. The forged steel was quenched and double tempered in order to achieve a maximum hardness of 22HRC, according to material requirements stated in NACE MR 0175 – ISO 15156 standards. The so heat treated steel was characterized by an ultimate tensile strength (UTS) of 760 MPa, a 0.2% yield strength of 618 MPa and an elongation at break of 24% as evaluated on tensile test specimens obtained from the same forging disk.

### 2.2. Corrosion test set-up

Samples were tested in open circuit potential (OCP) condition under tensile stress by means of a dead weight type machine. The stress applied to the specimens was equal to 80% of the 0.2% yield strength of the material. Corrosion tests were performed in a modified NACE TM0177 standard solution at room temperature and consisting in a 5.0 wt% ( $85.4 \times 10^{-2}$  M) NaCl, 2.5 wt% glacial acetic acid ( $\text{CH}_3\text{COOH}$ ) (standard NACE TM0177 test solution B) and  $10^{-2}$  M sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution in distilled water. Final pH solution was 3.2 and a  $[Cl^-]/[S_2O_3^{2-}]$  molar ratio of 85.4 resulted.

Test solution was continuously deaerated by nitrogen gas bubbling until AE recording started. Test cell was then sealed to avoid air inlet. Open circuit potential (OCP) of specimens after 5 min from immersion was about  $-0.600$  V<sub>Ag/AgCl</sub>. At the end of the test the OCP was more anodic and stabilized at about  $-0.540$  V<sub>Ag/AgCl</sub>. AE signals were recorded by a 10-channel Vallen AMSY-5 measurement system for the full period of the test. The acquisition was performed by using two sensors placed at the two ends of the sample. A third sensor has been employed as a guard sensor, connected to an independent block and it was used to acquire all the noise signals that were then removed during the data post processing. Details on the AE sensor positioning and test set up are described in [42]. AE sensors were piezoelectric transducers with high sensitivity (suitable for metal integrity testing), VS150-M type, that worked in 100–450 kHz frequency range with resonance at 150 kHz. In the experimental set-up, the thresholds of amplitude and rise-time parameters were set at 26.7 dB and 0.4  $\mu\text{s}$  respectively, the rearm time, which defines when the channel shall be ready to generate a new hit data set, was fixed at 3.2 ms, the duration discrimination time, which defines the detection of the end of the hit, was set at

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