

EVALUATION OF AND COMPARISON THE GENERAL CORROSION BEHAVIOR OF LOCALLY PREPARED SULFAMIC, AT 298 K.⁺

Lamy~a M. Dawood*

Abstract

The aim of this study is to investigate ,and compare the general corrosion behavior of the locally prepared sulfamic acid (HSO_3NH_2) . Three different alloys were used , commercially pure copper , AISI 1010 plain carbon steel , and AISI 316 Stainless steel Simple immersion test was performed on each of the above mentioned alloys, in two different concentrations of 5% , and 10% by weight(wt) , 99% purity of locally prepared sulfamic acid of pH (0.4- 0.6 at), 298K for 120 hr to evaluate corrosion rate by Mil per year (MPY) . For comparison purposes Annlar Sulfuric acid and Hydrochloric acid also were used at the same concentrations of 5%, and 10% by wt, at 298K using the same above mentioned alloys , for 120hr immersion duration. The tests indicates that the general corrosion rate for all the tested three alloys, in locally prepared sulfamic acid is far less (Minimum MPY values) than that for HCl and H_2SO_4 , especially for commercially pure copper and AISI 1010 carbon steel. These results are related to the formation of complex water-soluble sulfamate salts for each alloy used during corrosion reaction. While the formation of precipitated corrosion product salt layers causes further corrosion on using each of H_2SO_4 or HCl acids. This means that sulfamic acid can be used to replace safely H_2SO_4 and Hcl acid whenever the tested alloys are found at the different industrial applications. For AISI 316SS. Alloy the MPY values are (0.1 MPY at 5% wt, and 0.15 value at 10% wt) in locally prepared sulfamic acid although these values are lower than MPY values when immersing the same alloy is immersed in sulfuric acid . But still MPY values in sulfuric acid are fairly close. This means that sulfuric acid is still competitive to sulfamic acid on using alloy AISI 316SS.

المستخلص

لغرض تقييم السلوك التآكلي لبعض السبائك في حامض السلفاميك المحضر محليا تم استخدام ثلاث سبائك مختلفة هي النحاس ذو النقاوة التجارية ، الفولاذ الكربوني البسيط نوع AISI 1010 والفولاذ المقاوم للصدأ نوع AISI 316 . تم إجراء اختبار الغمر البسيط في درجة حرارة 298 K ولمدة 5 أيام (120hr) في حامض السلفاميك المحضر محليا وبنقاوة قدرها 99% وبتراكيزين مختلفين هما 5% و 10% وزنا بالتتابع لاستخراج معدل التآكل العام مقاسا بـ (MPY) Mil/Year ولكل سبيكة وتركيز على حدة. علما أن الحامضية pH لهذا الحامض كانت ما بين (0.4- 0.6) . للمقارنة بين السلوك التآكلي لحامض السلفاميك المحضر محليا والحوامض الأخرى تم استخدام كل من حامض الكبريتيك H_2SO_4 وحامض الهيدروكلوريك HCl القياسية Annlar ولنفس السبائك المستخدمة

⁺ Received on 9/6/2004 , Accepted on 10/11/2004

* Lecturer / Dept . Of Production And Metallurg Engineering University Of Technology

أعلاه وعند نفس الظروف (أي بدرجة حرارة 298 K ولمدة 120 ساعة وبالتركيز بين 5% و 10 % وزنا لكل حامض). وتبين من هذه الدراسة ان اقل معدل تآكل مقاسا بـ MPY كان عند الغمر في حامض السلفاميك المحضر محليا ولكل من السبائك الثلاثة المستعملة في هذه الدراسة. ولكن قيم MPY لكل من سبيكتي الفولاذ الكربوني وكذلك لسبيكة النحاس ذات النقاوة التجارية كانت اقل بكثير من تلك القيم المستحصلة لمعدلات التآكل المقاسة عند الاختبار في كل من حامض الهيدروكلوريك والكبريتيك. يمكن أن يعزى ذلك إلى إن الأملاح المتكونة كنواتج للتفاعل ألتا كلي عند الفحص (الغمر) في حامض السلفاميك ولكل السبائك المستعملة هي أملاح متكونة من مركبات معقدة ذائبة تماما في الماء. بينما الأملاح المتكونة في الحوامض المستخدمة لغرض المقارنة (أي حامض الهيدروكلوريك والكبريتيك) تكون نواتج تاكليه راسبه وذات تركيب كيميائي مختلف مسببة استمرار التآكل. إن هذا يعني ان بالا مكان استخدام حامض السلفاميك في الاستخدامات الصناعية بدلا من كل من الحوامض المذكورة للسبيكتين المذكورتين أعلاه. أما فيما يخص لسبيكة الفولاذ المقاوم للصدأ AISI 316 فعلى الرغم من إن قيم MPY في حامض السلفاميك اقل (MPY بقيمة 0.1 عند 5 % و MPY بقيمة 0.15 عند 10 % وزنا)، ولكن قيم MPY عند الغمر في حامض الكبريتيك ولهذه السبيكة لاتزال مقاربه لتلك القيم، مما يعني إمكانية استخدام حامض الكبريتيك مع سبيكة AISI 316 من الفولاذ المقاوم للصدأ .

Introduction

Many published literature show that sulfamic acid is a strong acid well – suited for many industrial applications , as scale remover, in chemical cleaning operations [1-2] for evaporators , super heaters , industrial boilers , condensers . Also sulfamic acid may be used in electroplating, water treatment, paper – pulp bleaching and many different important applications [1,3,4,5] .

Sulfamic acid is readily reactive with most deposits to form highly water soluble complex compound, thus minimizing the effect of the precipitated corrosion products on a metal or alloy [6, 7].

Sulfamic acid reaction with metal is as in the following equation [8]:-



M : Any metal except (As , Bi , Sb) , while Hg only forms precipitated salt [1 , 8]

Although sulfamic acid is strong, it is of low corrosion rate compared with other strong acids [1] , and this corrosion rate could be decreased further by the addition of an inhibitor [1 , 9] . Because of all its previous benefits, sulfamic acid with 99% purity was producedly[10] from local raw materials .

The aim of this research is to investigate the corrosion rate in MPY of the locally prepared acid since this acid has not been used yet in our country. So in this study some alloys that may find applications in industrial equipments, valves, pipe network or tanks... etc., were used.

Also comparison tests wen performed to study the possibility of replacing locally prepared sulfamic acid with traditional strong acids that are used in many industrial applications.

Experimental procedure

The chemical composition of the three alloys used in this research (AISI 316 SS, AISI 1010 plain carbon steel, and commercially pure copper), is listed in Table (1) Spectrometric technique was used .

Table(1): The chemical composition of the alloys tested

Element %Alloy	Cu	C	Mn	Si	S	Ni	Cr	Mo	Fe
Commercially Pure Copper	9999	Rem.
AISI 1010 Carbon steel	---	0.1	0.34	0.12	0.04	---	---	Rem.
AISI 316 SS.	0.7	0.018	1.79	0.69	0.03	12.27	16.27	2.13	Rem.

Also three different acids were used, 99% purity of the locally prepared sulfamic acid, and the properties of this acid are listed in Table (2) as indicated in ref [10].

Table(2): Properties Of locally prepared Sulfamic Acid[1\]

property	Value
Melting Point	203 °C
Purity	99%
pH	
Solution. wt 5 %of	0.65
% 10 Wt Solution.	0.4
Specific Conductivity ms/Cm	
Of 5% wt	29.4
Of 10% wt.	48.3
Water Solubility At 25 °C	21gm/100gm
Density	2.1gm/Cm

For corrosion evaluation of this acid (HSO_3NH_2) with the alloys tested two different concentrations of (5% ,10%) by weight of this acid were also prepared using deionized water.

Two strong familiar descaling acids were used to compare the corrosion of these acids with that of the locally prepared sulfamic acid, using the same alloys, these acids are:-

Analar Sulfamic acid (H_2SO_4) , and analar Hydrochloric acid HCl. Concentrations of 5%, and 10% by weight of these two acids were prepared using deionized water. All the tests were performed at 298K temperature. Standard preparation method was followed for preparation of 18 specimens (six specimen from each of the selected 3 alloys) .

The preparation of each specimen includes cutting, grinding using emery papers, and polishing with alumina of (0.5 Micron) in order to have similar surface finish for the 1 cm^2 area specimen.

Each specimen was immersed in the selected acid concentration for 120hr at 298k (= 3) temperature , in order to evaluate the difference in weight (before, and after the test) , in order to determine the general corrosion rate in MPY for each specimen , MPY was calculated using the equation [7].

$$MPY=543W/DAT \dots\dots\dots (2)$$

W: weight loss in mg, D: density of the specimen in gm/cm³
A: area of the specimen in square inch, and T: exposure time in hours.

Results And Discussion

All the results of our test on the corrosion rate for the three tested alloys in MPY is shown in Table (4). The test were made on the three used acids at 289K temperature using locally prepared sulfamic acid, and the two other acids that were used for comparison purposes they were sulfuric acid and hydrochloric acid.

From this table it could be noticed that :

1.For commercially pure copper alloy

As shown in Table (4) (1st row) that the maximum corrosion resistance minimum MPY values) is 1.93 MPY at 5% wt, 2.31 MPY at 10% , when this alloy is immersed in locally prepared sulfamic acid . This result may be related to the formation of complex stable and water soluble sulfamate salt [1,8].

The maximum MPY values that indicate minimum corrosion resistance results when this alloy is immersed in HCl acid (10.4 MPY value at 5% wt, and 5.8 MPY at 10%). These results may be related to the chloride ions that can be taken into the cuprous oxide film on copper to replace oxide ions and create cuprous vacancies that permit easier diffusion of cuprous ions through the film and increases corrosion rate [6,12].

When commercially pure copper alloy is immersed in sulfuric acid the formation of sulfate salt layer on the alloy surface and the increase in the oxidizing concentration increase the corrosion rate (MPY value increases from 4.32 at 5% wt to 5 at 10%wt) [7,8]. These results indicate that locally prepared sulfamic acid could replace efficiently both sulfuric and hydrochloric acids , whenever commercially pure copper is used.

2.For AISI 1010 Carbon Steel

The results in the 2nd row of Table (4) show that MPY values increase as the concentration of the three acids used increases. This is related to the increasing amount of hydrogen ions in each corrosion reaction [8]. But still when this alloy is immersed in locally prepared sulfamic acid the minimum MPY values are obtained {3.68 MPY at 5% wt ,and 4.14 MPY at 10% wt}. When immersing alloy AISI 1010 carbon steel is immersed in HCl MPY values are at maximum values in our study {10.1 MPY at 5% wt HCl, and 23.0 MPY at 10% wt HCl}. These value are expected since HCl is more active than sulfuric acid at equivalent concentrations and temperatures [11] and produces ferric ion that increases the metal (alloy) attack [6,7,11].

When carbon steel alloy AISI 1010 is immersed in sulfuric acid the MPY values increases from 8.75MPY at 5% wt to 9.67 MPY at 10% wt, the effect of sulfuric acid on iron and steel studied [13,14], and it was reported that the supersaturating of the solution adjacent to iron causes the formation of ferrous sulfate [13,15].

The precipitation on iron surface begins as clusters and nucleated in a way that the surface is covered porous layer that will permit further corrosion of this alloy [14].

These precipitated layers not found in the case when the same alloy is immersed in locally prepared sulfamic acid due to the formation of stable ,water soluble iron sulfamate layer[1,8].

3.AISI 316 SS.

Stainless steels are covered by coherent air formed passive layer of chromium oxide of high corrosion resistance and different chemical composition [6,7,16].

Table (4) {3rd row} also indicates that sulfuric acid is still competitive to sulfamic acid in the tested concentrations for AISI 316 SS alloy at 298K. The minimum MPY values also were recorded in immersing this alloy in locally prepared sulfamic acid {0.1 MPY at 5% wt , and 0.15 MPY at 10% wt}. On the other hand, the maximum values were obtained on immersing in HCl acid {2.85 MPY at 5% wt, and 2.08 at 10% wt}. It is reported [16] that the passive layer that is formed on stainless steels in chloride environments are of duplex layer, the outer layer is porous and amorphous .

The channels that form on the outer layer allow large anion to move towards the lower less dense inside layer causing pitting corrosion , such aggressive anions as (Cl ,I,..etc) [16]. The metal loss is small in pitting corrosion compared with the damaged surface [7], that is why the MPY values decrease on increasing HCl concentration for stainless steel alloy 316 SS. Results that are obtained when SS.,alloy is immersed in sulfuric acid show the corrosion process is increased as the oxidizing power increases [7].

These MPY values although they are higher than those obtained in sulfamic acid , are still quite acceptable (0.15 MPY at 5% wt, and 0.20 MPY at 10%wt).

Since it is reported that the metal resists corrosion if MPY value is less than one [7,17] so sulfuric acid is still competitive to sulfamic acid when stainless steel alloys are used. The trend of our results is similar to that reported in ref [8] on sulfamic acid behavior with different alloys. This is shown in Table (3) in their relative conditions [8].

Table(3): Relative Corrosion Rates[2] Of 3% Aqueous Solution Of Acids
At 22= 2 C; Sulfamic Acid=1

Metal	sulfuric Acid	HCl
Steel 1010	2.6	4.2
Cast Iron	3.2	3.2
Galvanized Iron	63.0	very rapid corrosion
Tin Plate	81.0	23.0
304 Stainless Steel	10.0	very rapid corrosion
Zinc	2.2	very rapid corrosion
Copper	1.5	6.7
Brass	1.5	2.8
Bronze	4.0	7.0
aluminum	0.6	5.3

Table(4): Results Of This Study

Element % Alloy	Corrosion Rate MPY*					
	Sulfamic Acid 5%wt 10%wt		Hydrochloric 5%wt 10%wt		Sulfuric Acid 5%wt 10%wt	
Commercially Pure Copper	1.93	2.31	10.4	5.8	4.32	5
AISI 1010 Carbon steel	3.68	4.14	10.1	23.0	8.75	9.67
AISI 316 SS.	0.1	0.15	2.85	2.08	0.15	0.20

*At 298K(= 3), for 120hr.

Conclusion

1. Tested alloys show high corrosion resistance (lower MPY values) in locally prepared sulfamic acid due to the formation of water soluble and stable sulfamate salts . Future studies on may be needed at different test temperatures.
2. Locally prepared sulfamic acid may replace efficiently HCl and H₂SO₄ acid in industrial applications whenever carbon steel AISI 1010 and commercially pure grade copper alloys are used .
3. Further studies on the effect of inhibitor addition in locally prepared sulfamic acid is required .

References

- 1-L.E Audrieth et.al , *J . chem . Review*, 26,49 ,1946.
- 2- L.James,*Encyclopedia of Chemical Technical Technology* , 1978.
- 3- www.lane – 90v , 2002 .
- 4- www.mineral social . org /bultenin/ htm , 2002.
- 5- [www.brentlae.be / prd/ product/htm/](http://www.brentlae.be/prd/product/htm/) , 2002.
- 6- *Www.Supply system .ussa .com / doce/ dsy.htm* , 2002.
- 7- T.kuno and Y.kanagama,U.S.patent 5346643 ,1994.
- 8- L.George U.S patent, 69224 , 1987.
- 9- H.H. Uhlig and R. Winston Revie *Corrosion and Corrosion Control*, 3rd ed. John Wiley and sons ,1985.
- 10- Mars.,G.Fontana, and Norbert., D .Greene *Corrosion Engineering* McGraw - Hill Book Company, 1979.
- 11- A.M.Ali et.al . *J.Of Eng. & Tech.* Nov. 2004.
- 12- *www.Physical and Ttheoretical lab. Safety* , 2001.
- 13- North,R.,F, and Pryor, M., J., *Corro.,Sci.*, 10,297, 1970.
- 14- L.Shreir “ Corrosion “ ,Vol.2., *Butterworth and Co* (publishers)ltd.2nd edition,1963.
- 15- Muller,W.,J.,*Faraday SOC.*,39,737, 1931.
- 16- Serra and Feliu., Int. “Committee of Electrochemical Thermodynamics And Kinetics”, 6th Meeting, London, pp 360, 1955.
- 17.Krstulovic et.al,*Corro.Sci.*, 21, 95, 1981.