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A comparative kinetic study of common metals scavenging efficiency for aqueous sulfide pollutants in seawater

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ABSTRACT

A comparative study was made in order to estimate the feasibility of using common metal alloys shavings for low level sulfide removal from seawater under aerated and deaerated conditions. Six different metals and alloys were used in the form of shavings. A batch recycle reactor with a large recycle ratio was utilized for this purpose. Generally all the heterogeneous systems performed better than the homogeneous reaction. The presence of oxygen, can significantly improve the effectiveness of these metals and alloys shavings in removing pollutant. In the diffusion region, in deaerated conditions, the mass transfer coefficient was estimated. In aerated condition the reaction was under activation control. The batch recycle reactor containing the shavings with large recycle ratio was shown to approximate ideal stirred tank reactor in the diffusion regime. Activation energies in the diffusion regime were low as expected (i.e. 1-2 Kcal/mole). The assumed reaction order for both the diffusion and the kinetic regime were confirmed by comparing the experimental with the calculated half life. It is found that increasing the concentration of sulfide doesn't change the order of reaction. Copper has shown the best scavenging efficiency for sulfide removal with a half life time of about twenty five minutes.

Introduction

Sulfide is a common pollutants of water from industrial wastes and from bacterial reduction of sulfate [1]. Sulfide containing water causes odor nuisances especially in hot regions of the world, e.g. Kuwait [2]. In addition sulfide can cause severe deterioration of heat exchanger piping made of Cu/Ni alloys [3-5]. Furthermore, sulfide can cause serious corrosion of concrete sewers. Sulfide removal has become a task for many investigators [e.g. 6]. Various methods were utilized to remove sulfide using either homogeneous catalysis [e.g. 6] or heterogeneous catalysis [7] or heterogeneous electrochemical technique [8]. In the case of heterogeneous reactions, when seawater polluted with sulfide is passed through a packed bed of metal oxides, there are two possible modes of reaction. The first is the precipitating of metal sulfide as can be observed by a blackish color of copper sulfide

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precipitating. The second mode of possible reaction, is through the dissolution of metal ions in the solution thus making it possible for three modes of reaction to occur. In the first, the metal ions will react homogeneously forming a non soluble metal sulfide by thermodynamic constraint. The second reaction is the catalysis of metal ions for sulfide oxidation which are often reported [9]. The third mode of reaction is the direct catalytic reaction at the solid surface.

In this research, it is attempted to investigate the potential ability of six different common metals and alloys shavings in removing sulfide in aqueous environment. In Table 1, the weights and porosity of these metal shavings are indicated. In this research project, it is aimed at investigating the hydrodynamic factors, sulfide level and activation energy.

The investigation was carried out using a batch recycle reactor which are commonly used in the industry for rate determination from experimental measurement [10].

Experimental Procedure

Batch - recycle reactor are frequently used to establish rate equations from experimental measurements (Smith [10]). The experimental set up for the batch - recycle reactor is shown in Fig. 1. In this figure the volume of the tank was 20 liters containing seawater which was prepared by using industrial grade sodium chloride (3.4%). The tank was connected to a pump which circulate the seawater through a packed bed reactor. The packed bed reactor consist of three equal size cylindrical stages (0.8 liter/stage). The flow rate was adjusted to 4.2 liters/minute. Mixing in the tank was accomplished by using two heavy duty magnetic stirrers (400 rpm). Aeration or deaeration was done by bubbling air or nitrogen respectively at 2 psig pressure and room temperature. Experiments were performed at 20 ^{o}C unless otherwise specified. Two flow conditions were investigated and were classified as 100% flow (250 liters/hour) and 50% flow (125 liters/hour). The pipe diameter used was 11.6 mm. In the homogeneous oxidation experiment, the reactor was empty. While in the other experiments, the alloys shavings or glass beads were packed in the middle cylindrical stage of the reactor. In the glass beads experiment, the glass beads were 0.5 cm in radius. Glass beads experiments were done for comparative reasons of providing a non catalytic surface for the reactions. Sulfide concentration were measured by iodimetric method and were also confirmed using fuchsin (basic) method from predetermined calibration curve using spectrophotometer. In the fuchsin method sodium tri-poly-phosphate was added to stabilize the sulfide concentration. The analar grade sodium sulfide was used to prepare the initial sulfide concentration of 2 ppm. This concentration of sulfide was used in all the experimental tests. An additional initial sulfide concentration of 10 ppm was investigated. Six different types of commonly available alloys were made into shavings and are listed in Table 1.

Results and Discussion

The initial and change in pH for sulfide system is shown in Tables 1. In all cases in this investigation the pH decreased, thus indicating the production of hydrogen ions. A pH change of as a large as 2.1 indicates significant change in the pH of solution. It is interesting to note that the change in pH for different metal oxide are different due to the different reaction mechanism. This dependent on the number of hydrogen ions produced per molecule of pollutant reacted. A low pH change (e.g. 0.4 for homogeneous reaction) can be attributed to probably low number of hydrogen molecules produced. For example, brass results in a two fold drop in pH, which can be attributed to different reaction mechanism. In this case, for deaerated solution there is twice as much hydrogen ions produced per pollutant as compared to aerated solution.

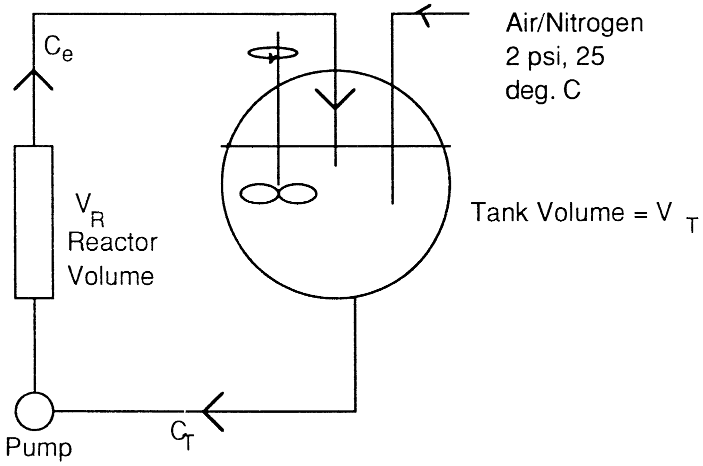

Fig. 1. The batch-recycle reactor utilized in the present investigation.

Table 1. Experimental parameters of the investigated catalysts in deaerated and aerated sulfide polluted seawater.

Type	Weight (grams)	Porosity %	Deaerated		Aerated	
			Initial pH	ΔpH	Initial pH	ΔpH
Homogeneous	0.0	100	9.15	-0.4	9.2	-0.45
Glass Balls	938.7	64.7	9.2	-0.7	9.2	-0.7
Copper	247.3	26	9.1	-1.6	9.3	-1.6
Copper Oxide	247.3	26	8.6	-1.6	9.1	-0.7
Brass	267.8	34	8.5	-2.3	8.2	-1.1
Mild Steel	253.4	10.6	8.2	-0.9	7.3	-0.9
Aluminum	355	18	8.7	-1.5	8.6	-1.8

Thus the deaerated reaction mechanism produce two ions of hydrogen per molecule of pollutant, while aerated solution produce one molecule of hydrogen. However, for example, in the copper system, equal pH change is observed, which

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means in aerated and deaerated system one molecule of hydrogen is produced per molecule of pollutant. This could be due to the fact that oxygen was consumed by copper to produce copper oxide and thus aeration does not affect the reaction mechanism. In contrast to this is the copper oxide system, where the pH change in deaerated solution was twice as large as aerated, which reflect the effect of oxygen on the reaction mechanism, since it is unlikely copper oxide can react with oxygen.

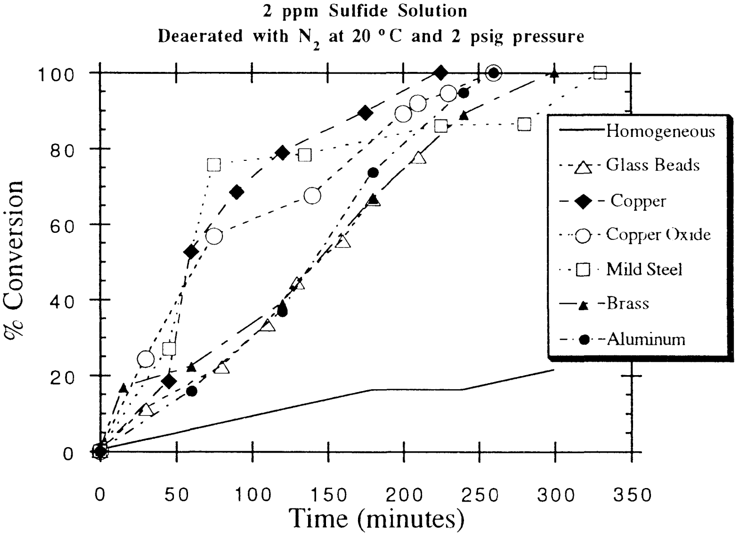

Fig. 2. The performance of the metals in removing the sulfide at room temperature in deaerated polluted seawater for 100% flow.

The conversion versus time curves, which are shown in Figures 2 and 3, have shown reaction kinetic orders between zero and one, with respect to sulfide. The alloys are ranked according to their scavenging effectiveness as determined by comparing the corrected rate of reaction based on equal porosity. In Table 2, the ranking of the alloys investigated are shown for sulfide polluted seawater under aerated and deaerated solutions. It is clear from Table 2, that copper ranks best in aerated solution while mild steel ranks best for deaerated solution. It is interesting that , aluminum ranks second best for both aerated and deaerated solution. The experimental half lives for sulfide removal are shown in Table 3 and 4, where they are compared to the calculated half lives which are based on determined order of the reaction with respect to sulfide [10]. The assumed mechanism of reaction is correct as it can be seen by comparing the calculated and experimental half lives. It is clear that copper in aerated solution can remove 50% of low levels of dissolved sulfide at 30 °C in about 25 minutes.

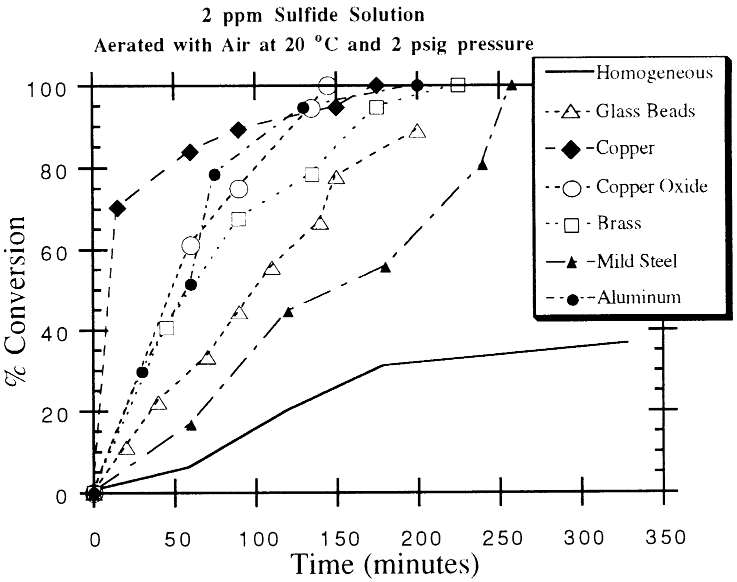

Fig. 3. The performance of the metals in removing the sulfide at room temperature in aerated polluted seawater for 100% flow.

Table 2. The ranking of metal shavings for their scavenging effectiveness of pollutants in seawater.

Rank	Aerated	Deaerated
I	Cu	Mild Steel
II	Al	Al
III	CuO	Cu
IV	Mild Steel	Brass
V	Brass	CuO
VI	Glass Beads	Glass Beads
VII	Homogenous.	Homogenous

Table 3. A comparison of the calculated and experimental half lives for the various systems investigated under deaerated conditions. For zero order reaction multiply the velocity constant (gmole/liter/min) by 10^7 and for first order reaction multiply the velocity constant (min^{-1}) by 10^3.

Parameters				Experimental $t_{1/2}$ (min)		Calculated $t_{1/2}$ (min)	
Type	Flow %	$S^=$ ppm	React. Order	293.16 °K	303.16 °K	293.16 °K	303.16 °K
Glass Beads	100	2	0	140	125	134	120
	50	2	0	163	176	161	152
Copper	100	2	1	99	80	105	65
	50	2	0	203	141	207	160
Copper Oxide	100	2	1	73	▨	66	▨
	50	2	1	94	▨	82	▨
Aluminum	100	2	1	75	60	69	60
	50	2	0	128	108	150	103

Table 4. A comparison of the calculated and experimental half lives for the various systems investigated under aerated conditions. For zero order reaction multiply the velocity constant (gmole/liter/min) by 10^7 and for first order reaction multiply the velocity constant (min^{-1}) by 10^3.

Parameters				Experimental $t_{1/2}$ (min)		Calculated $t_{1/2}$ (min)	
Type	Flow %	$S^=$ ppm	React. Order	293.16 °K	303.16 °K	293.16 °K	303.16 °K
Glass Beads	100	2	0	99	79	109	103
	50	2	0	160	95	141	129
Glass Beads	100	10	0	77	▨	83	▨
	50	10	1	160	▨	151	▨
Copper	100	2	1	34	24	36	26
	50	2	0	74	70	71	66
Copper Oxide	100	2	1	43	▨	49	▨
	50	2	1	43	▨	51	▨
Copper Oxide	100	10	1	15	▨	36	▨
	50	10	1	134	▨	105	▨
Aluminum	100	2	1	60	40	54	31
	50	2	0	100	60	140	88

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Table 5. The velocity constant for an assumed first order kinetic for the various conditions investigated for a 2 ppm sulfide polluted seawater.

Type	$K_1 \times 10^5$ (1/sec) 50% Flow Conditions				$K_1 \times 10^5$ (1/sec) 100% Flow Conditions			
	Aerated		Deaerated		Aerated		Deaerated	
	20 °C	30 °C	20 °C	30 °C	20 °C	30 °C	20 °C	30 °C
Glass Beads	5.9	6.5	5.2	5.5	7.7	8.1	6.2	6.9
Copper	11.8	12.6	4.0	5.2	12.7	17.6	6.1	7.2
Copper Oxide	9.0		6.5		9.9		7.8	
Mild Steel					8.6		4.6	
Brass					5.5		5.8	
Aluminum	5.9	9.6	5.6	6.4	10.3	18.7	6.6	7.6

Table 5, shows the velocity constant for an assumed first order kinetics under the various conditions investigated for a 2 ppm sulfide polluted seawater. It can be seen that the velocity constants under deaerated conditions are around 5.0 $\times 10^{-5}$ (1/sec) independent of the flow rate and temperature as well as the type of material investigated. This is definitely a diffusion control reaction and thus the determined velocity constant is the mass transfer coefficient of the system. In support of this, is the low activation energy for most of the systems tested which means that the mass transfer coefficient is not significantly changed as a result of a 10 degrees change in temperature (i.e. 20 to 30 °C). In aerated condition the velocity constant is highly dependent on the flow rate as can be readily observed in Table 5. It is also clear in Table 5 that in aerated conditions the velocity constant values are generally higher and are more sensitive to temperature variations which indicates an activation control reaction. In support of this is the data shown in Tables 3 and 4 in which the experimental half live are compared to the calculated half life based on first order kinetic. It is clear that the assumed reaction kinetics are fairly reasonable. It can be seen in Table 5 that in all cases at 100% flow the reaction rate for metal and metal oxide are much higher than for the case of glass bead which indicate the catalytic effect of these metals and metal oxides. For example, for 100% flow and aerated solution at 30 °C, copper is about three times more efficient than glass beads.

Reaction Kinetics

Hydrogen sulfide is oxidized through homogeneous reactions in the presence of oxygen as follows [11]:

$$HS^- + 2O_2\ (aq) \rightarrow HSO_4^-$$

$$2HS^- + 3O_2\ (aq) \rightarrow 2HSO_3^-$$

$$2HS^- + O_2\ (aq) \rightarrow S_2O_3^{=} + H_2O$$

$$2HS^- + \tfrac{1}{2}O_2\ (aq) \rightarrow 2S^0 + H_2O$$

At higher pH, which is the case investigated, the formation of sulfur is not favored, and thus no poly-sulfides are formed [12]. Two possible reaction mechanisms can be postulated and can be classified as either catalytic or non-catalytic. However for both postulated mechanisms, the mechanism must take into account the production of hydrogen ions. Thus, for non-catalytic reaction mechanism the following sequence of reactions take place:

1 - Sulfide can react with the metal surface to form precipitated metal sulfide.
2 - The electro-neutrality of the solution will be violated. This will induce the production of hydrogen ion.
3 - The number of hydrogen ion produced depends on the metal type.

This mechanism is supported by the fact that most metal sulfides have low solubility. A catalytic mechanism is possible, through :

$$S^{=} + H_2O\ \ (aq)\ \xrightarrow{\text{catalyst}}\ S_2O_3{}^{=} + 2H^{+}$$

for sulfide pollutant. These reactions will be accompanied by another chemical reaction at the surface to balance the electrons such as:

$$2Fe(III) \longrightarrow 2Fe(II) \text{ for mild steel shavings or}$$

$$Cu(II) \longrightarrow Cu \text{ for copper and copper oxide.}$$

Reactor Analysis

As shown by Smith [11] the condition for the present batch recycle reactor to be considered as differential reactor is that the rate of reaction is given by:

$$r = \left(\frac{V_R+V_T}{V_R}\right)\frac{-dX}{dt}C_0$$

$$C_T - C_e = -\frac{V_R}{Q}\left(\frac{V_T}{V_R+V_T}\right) r \qquad \text{for } (C_T - C_e) \rightarrow 0$$

Smith [10] concluded that the assumption of a differential reactor operation is valid, provided that $\frac{V_R}{Q}$ is small. In this experimental investigation, the value of $\frac{V_R}{Q}$ is equal to 0.19. Thus, it can be assumed that our experimental set up approximate a differential reactor. In support of this, is the practically constant initial rate of reaction as shown in Figs. 2 to 5, where the slope of conversion versus time (e.g. $\frac{-dX}{dt}$) is practically constant. It is interesting to note that in Tables 2 for deaerated case and 3 for the aerated case, the half life of sulfide in the reactor was calculated based on resulted reaction order with respect to sulfide concentration. Generally, the experimental half lives agree fairly well with those calculated which were based on resultant reaction order kinetic with respect to the sulfide concentration.

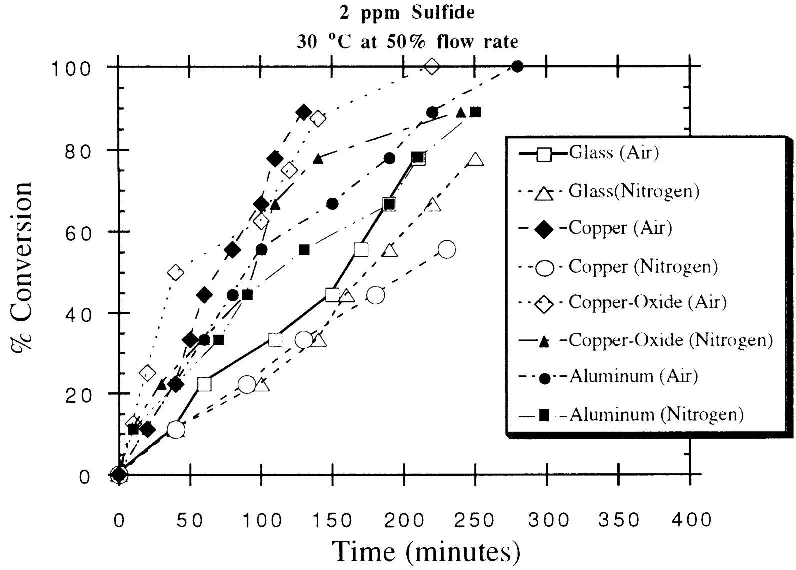

Figure 4. The performance of the metals in removing the sulfide at 30 ^{o}C in aerated/deaerated sulfide polluted seawater at 50% flow rate.

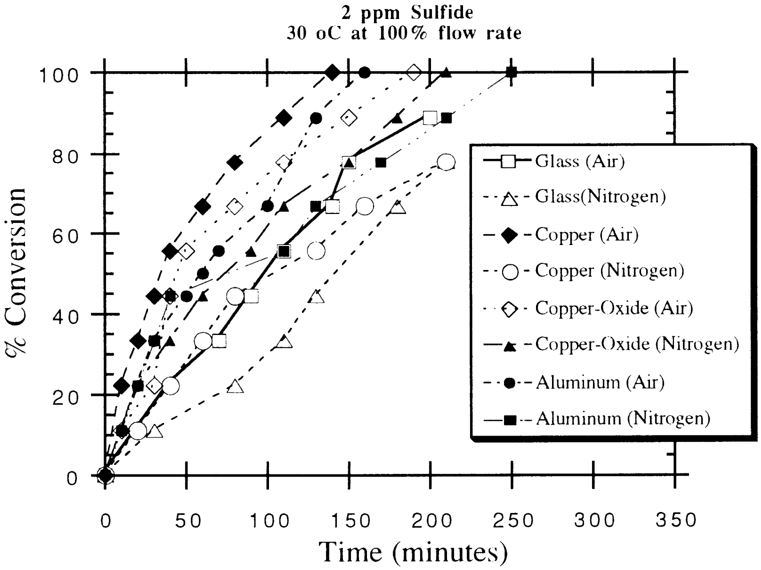

Figure 5. The performance of the metals in removing the sulfide at 20 ^{o}C in aerated/deaerated sulfide polluted seawater at 100% flow rate

According to Smith [10] the batch - recycle reactor with a very large fraction of recycle (i.e. 100% flow rate) approximate ideal stirred tank performance for the case where the reaction rate is under diffusion control. This was confirmed in the present investigation. Smith [10] derived the following constant volume equation for a batch stirred tank reactor (STR), i.e.

$$t = -\ C_0 \int_0^X \frac{dX}{r}$$

where, t is the time required to achieve conversion X. The above equation reduces to :

$$t = -\frac{C_0}{r} X$$

for the present investigation. For example, in any case where the reaction is under diffusion control (constant reaction rate), the predicted half life is about 156 minutes. This compares fairly well with the experimental half life shown in Tables 2 and 3.

Conclusion

1. The ideal system for the utilization of this finding is the scrubbing of hydrogen sulfide from waste gases. Thus the contamination of environment is minimized by an aqueous closed loop system.
2. The batch recycle reactor with large recycle ratio approximates an ideal stirred tank reactor in the diffusion region only.
3. The variation of flow rate has indicated two region of mass transport control reactions. In the diffusion region the mass transfer coefficient is around 5×10^{-5} (1/sec) and the calculated activation energy was in the range of one to two Kcal/gmole. In the kinetic region the reaction order with respect to sulfide was one and the reaction is very sensitive to the presence of oxygen and the activation energy was about 5 to 10 Kcal/gmole.
4. The presence of oxygen can significantly improve the scavenging effectiveness only in the kinetic region. In the diffusion region the reaction is independent of the concentration of oxygen.

Nomenclature

C_T = the sulfide concentration in the tank (gmole/liter).
C_e = the sulfide concentration at the reactor exit (gmole/liter).
C_0 = the initial sulfide concentration (gmole/liter).
K1 = velocity constant for a first order reaction.
Q = the volumetric flow rate liters/minute
r = he rate of reaction gmoles/(liter)(minute)
V_T = the tank volume (liters)
X = the fractional conversion.

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