Models of the Mass Loss of Some Copper Alloys

A. Barbulescu, C. S. Dumitriu

Ovidius University of Constanţa, Bd. Mamaia, 124, 900527, Constanţa, Romania
e-mail: abarbulescu@univ-ovidius.ro

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Abstract: In this paper we discuss about the corrosion mechanism of some copper alloys introduced in sour petroleum and we give mathematical models of the mass loss, function of time.

Keywords: liquid, gravimetric index, corrosion, mass loss

1. Introduction

The phenomena related to the erosion of materials produced in some liquid media are of major importance point of view of the alloys employed in industry. Ones of them are copper alloys, used in naval constructions of sour petroleum carrier.

Four such materials were studied. We shall discuss some aspects related to the mass loss of the alloys introduced in sour petroleum and the mechanism that explains the mass loss.

2. Experimental

The experiment made to determine the corrosion speed was fulfilled as follows: every sample of alloy was introduced in a vessel containing 150 ml of sour petroleum, for 97 days. At different time intervals the mass determination was made.

The petroleum used was of Siberian Light type, with density of 833 kg/m^3, with a low content of sulphur, (0.55% g), water (0.1% vol.) and sels (0.0005%), low acid (1.5 mg KOH/ 100g petroleum).

The studied samples of materials were:
- global copper (99.78% Cu, 0.0747 % Zn, 0.0395 % Fe, and 0.0446 Sn), with the mass of 11.7317 g;
- Cu – 20 – a base Pb brass (57.95 % Cu, 38.45% Zn, 2.75% Pb), with the mass of 12.5306 g;
- Cu – 60 – a base Pb bronze (83.09% Cu, 6.40 % Sn, 4.40% Pb, 4.07% Zn), with the mass of 17.2455 g;
- Cu – 70 – a base Al bronze (80.54 % Cu, 9.85% Al, 4.59% Fe, 4.40 % Ni), with the mass of 23.4462g.

3. Results and discussions

The registered mass variations (g) in time (days) are given Table 1 and are represented in Figs. 1-4.

It can be seen that after a mass decays in the first 20 days, the increasing of the samples mass were registered. It was due to the reaction compounds, that adhered on the samples surfaces.

This phase was followed by a stand off of those compounds, having as a consequence the mass decreasing.

TABLE 1. The mass variation, in sour petroleum

| Time (days)	Cu-20 (g)	Cu-60 (g)	Cu (g)	Cu -70 (g)
0	16.5635	27.8973	11.7499	18.2278
1	16.5635	27.8973	11.75	18.2285
4	16.5635	27.8973	11.749	18.2279
7	16.563	27.8976	11.7486	18.2274
11	16.5626	27.8978	11.7477	18.2269
14	16.5631	27.8979	11.7487	18.2273
22	16.5629	27.8983	11.7485	18.227
46	16.5658	27.8991	11.75	18.2284
56	16.5639	27.8987	11.7482	18.2273
67	16.5641	27.8978	11.7486	18.2272
77	16.5633	27.8974	11.7482	18.2269
90	16.5627	27.8970	11.7478	18.2264
97	16.5620	27.8968	11.747	18.2263
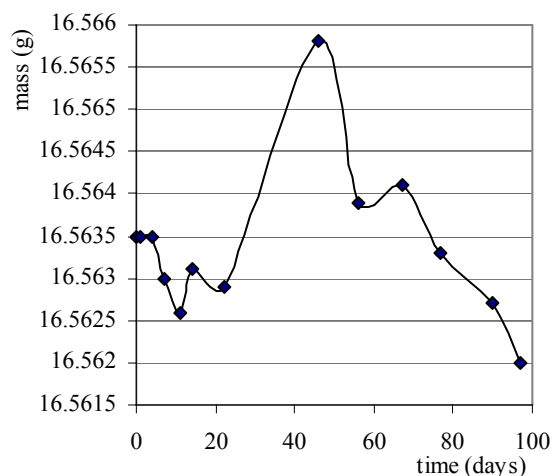
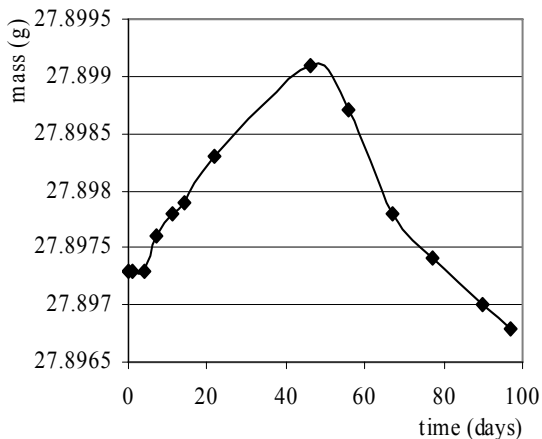Figure 1. The mass variation (g) of Cu-20 sample

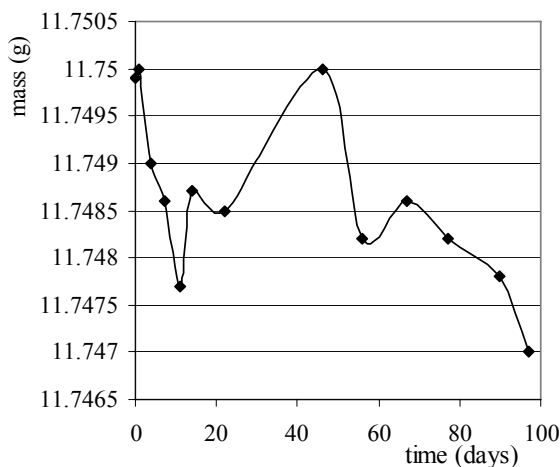Figure 2. The mass variation (g) of Cu-60 sample

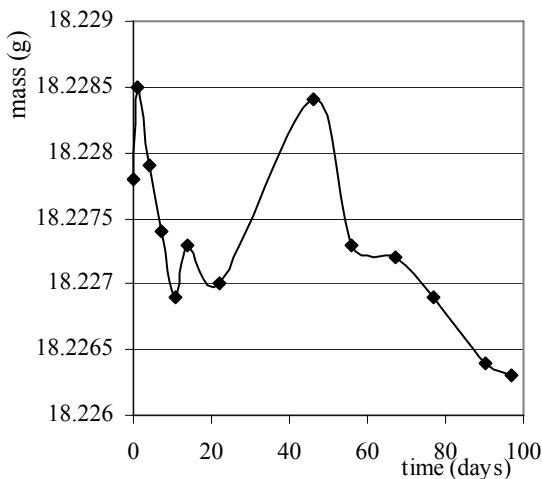
Figure 3. The mass variation (g) of Cu sample

Figure 4. The mass variation (g) of Cu -70 sample

Let us denote by:

$$\Delta m_i = m_0 - m_i$$

the absolute mass variation, where m_i is the mass at the momentul t_i, and m_0 is the mass at the moment $t_0 = 0$.

In order to compare the materials mass loss, the absolute mass loss on surface, were determined. The values are given Table 2 and are represented in Fig. 5.

TABLE 2. The absolute mass variation on surface in sour petroleum

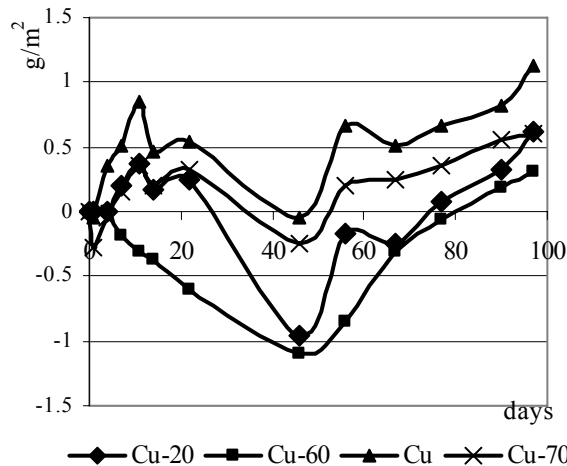| Time (day)	Cu-20 (g/m^2)	Cu - 60 (g/m^2)	Cu (g/m^2)	Cu -70 (g/m^2)
0	0	0	0	0
1	0	0	-0.0387	-0.2819
4	0	0	0.3480	-0.0403
7	0.2072	-0.1826	0.5027	0.1611
11	0.3729	-0.3043	0.8507	0.3624
14	0.1658	-0.3651	0.4640	0.2013
22	0.2486	-0.6085	0.5414	0.3221
46	-0.9531	-1.0954	-0.0387	-0.2416
56	-0.1658	-0.8520	0.6574	0.2013
67	-0.2486	-0.3043	0.5027	0.2416
77	0.0829	-0.0609	0.6574	0.3624
90	0.3315	0.1826	0.8120	0.5637
97	0.6216	0.3043	1.1214	0.6040

Figure 5. The graphs of absolute mass variation on surface in sour petroleum

The smaller absolute mass loss on surface was registered by Cu -70 and the biggest, by copper.

Using the data from Table 2, we determine the gravimetric indices, defined by:

$$i = \frac{\Delta m}{S \cdot \Delta t},$$

where:
- S is the total surface of the sample,
- Δm is the total mass loss,
- Δt is the time interval.

In our cases,

$$i_{Cu-20} = 0.227 \cdot 10^{-3} \, g/m^2 \cdot h,$$
$$i_{Cu-60} = 0.13 \cdot 10^{-3} \, g/m^2 \cdot h,$$
$$i_{Cu-60} = 0.4798 \cdot 10^{-3} \, g/m^2 \cdot h,$$
$$i_{Cu-70} = 0.2259 \cdot 10^{-3} \, g/m^2 \cdot h.$$

So, the most resistant alloy was the bronze Cu -60.

In order to present the mathematical models obtained for the mass loss on surface, in time, some mathematical concepts must be introduced [1].

If $(y_i)_{i=1,n}$ a data series, registered at the moments $(t_i)_{i=1,n}$ and f is a regression function, that describes the series evolution, in time, *the standard error of the estimate* is defined by:

$$s = \sqrt{\frac{\sum_{i=1}^{n}(y_i - f(t_i))^2}{n - m}}, \qquad (6)$$

where $f(t_i)$ denotes the function value calculated from the regression model and m is the number of parameters in the particular model.

The standard error of the estimate quantifies the spread of the data points around the regression curve. As the quality of the data model increases, the standard error approaches zero.

Another measure of fit quality is the correlation coefficient. It will be introduced using the *standard deviation*, defined by:

$$S_t = \sum_{i=1}^{n}(y_i - \bar{y})^2,$$

where $\bar{y}$ is the average of the data points, given by:

$$\bar{y} = \frac{1}{n}\sum_{i=1}^{n} y_i.$$

S_t quantifies the spread of the data around a constant line (the mean) as opposed to the spread around the regression model. This is the uncertainty of the dependent variable prior to regression.

We also define the deviation from the fitting curve by:

$$S_r = \sum_{i=1}^{n}(y_i - f(t_i))^2,$$

that measures the spread of the points around the fitting function.

Now, using S_t and S_r, the *correlation coefficient* is defined by:

$$r = \sqrt{\frac{S_t - S_r}{S_t}}.$$

This is not exactly the classical definition of the correlation coefficient, but it has the same property as the classical one.

As the regression model better describes the data, the correlation coefficient will approach unity.

Now, using the data given in Table 2, the equations of the mass loss on surface, in time, where determined. They were, respectively:
-    for Cu - 20:

$$\frac{\Delta m_i}{S} = -0.06288 + 0.06547 t_i - 0.00394 t_i^2 + 6.4 \cdot 10^{-5} t_i^3 -$$
$$- 3.07 \cdot 10^{-7} t_i^4,$$

with $s = 0.22712$ and $r = 0.87327$;
-    for Cu – 60:

$$\frac{\Delta m_i}{S} = 0.02143 - 0.01547 t_i - 0.00144 t_i^2 + 3.81 \cdot 10^{-5} t_i^3 -$$
$$- 2.21 \cdot 10^{-7} t_i^4,$$

with $s = 0.98592$ and $r = 0.08250$;
-    for copper:

$$\frac{\Delta m_i}{S} = 0.019404 + 0.08278 t_i - 0.00359 t_i^2 + 5.29 \cdot 10^{-5} t_i^3 -$$
$$- 2.43 \cdot 10^{-7} t_i^4,$$

with $s = 0.23170$ and $r = 0.84827$;
-    for Cu -70:

$$\frac{\Delta m_i}{S} = -0.17405 + 0.065743 t_i - 0.00304 t_i^2 + 4.72 \cdot 10^{-5} t_i^3 -$$
$$- 2.26 \cdot 10^{-7} t_i^4,$$

with $s=0.15275$ and $r = 0.88894$;

Since the standard errors of estimation are small and the correlation coefficients are close to 1, the models are well chosen. In all the cases, the fit functions were polynomials of forth order.

From the experiment it results that the corrosion speed was very small. It can be explained having in mind the alloys nature and the liquid used in experiment.

The principal components of sour petroleum are the hydrocarbons. It also contains other substances that have carbon, hydrogen, oxygen, nitrogen, metallic ions included in organic–metallic compounds. The compounds with O, S, and N are at the base of the chemical corrosion produced at the contact between the metals or metallic alloys with the sour petroleum.

Another component of the petroleum is the water (in small quantities) in which sells (NaCl, CaCl2, MgCl$_2$) are solved [2, 3]. The electrolyte solution is emulsified in sour petroleum and produces the destruction by corrosion, more pronounced at higher temperatures.

The corrosion probability in the environment conditions is small because the electrolyte solution is a disperse phase in the hydrocarbons phase. At high temperatures (120 - 130^0 C) and pressures (12 bar), the hydrocarbons viscosity decreases, the interfacial pressure also decreases and the drops of aqueous solution are easier deposited, such that the metallic surface will be exposed of the corrosion with an electrochemical mechanism.

The corrosion aspects described, due to the sells solved in the water associated to sour petroleum are of importance in petroleum transport at normal temperatures. The non-hydrocarbons – the compounds with nitrogen, oxygen and sulphur – are responsible to the corrosion produced by sour petroleum, even at reduced temperatures.

The sulphur exists in an elementary form and is very corrosive. Especially corrosive are also some compounds with sulphur, as H$_2$S and the mercaptan, the organic sulphides, the disulphide, etc [4].

The elementary sulphur, the hydrogen sulfide and the mercaptans produce the corrosion following a chemical

mechanism, by the direct reaction between them and some metals. The copper is given as an example [5].

The compounds with oxygen most susceptible to produce corrosion are the petroleum acids [4]. Between them, the aliphatic acids have the biggest acidity, being the most corrosive. The corrosion produced by them is a chemical one.

The compounds with nitrogen from sour petroleum (especially those that exhale ammonia vapors at heating) can also produce a chemical corrosion, by a mechanism described in [6]. The ammonia attacks copper, forming complex compounds, in favorable conditions, as a temperature greater than 100^0C.

4. Conclusions

In this paper we gave mathematical models that describe the mass variation in time, for some copper alloys introduced in sour petroleum and to discuss the experimental results.

It was proved that the absolute mass loss can be described in all the studied cases by polynomials of forth degree.

Since the sour petroleum used for experiment had a small acidity, the corrosion speed was very low.

The studied samples of brass, copper and bronzes suffered a chemical due to the presence of the sulphur, of some sulphur compounds (hydrogen sulphur, mercaptans) and of petroleum acids.

Also, a passivation of the copper and its alloys were observed – having as a effect a small increasing of the samples mass, at the experiment beginning, followed by a mass stabilization.

REFERENCES

1. Hyams D., Curveexpert 1.3. Help, Copyright 1995-1997
2. Suciu G., Ingineria prelucrării hidrocarburilor, vol. III, Editura Tehnică, Bucureşti, **1993**
3. Tănase I., Analiză instrumentală. Metode electrochimice de analiză, Ed. Tehnică, Bucureşti, **1992**
4. Koncsag C., Fizico – chimia petrolului, Ovidius University Press, Constanţa, **2003**
5. Neniţescu C., Chimie generală, Editura Didactică şi Pedagogică, Bucureşti, **1977**
6. Zamfir S., Vidu R., Brînzoi V., Coroziunea materialelor metalice, Editura Didactică şi Pedagogică, Bucureşti, **1994**