Silver braze corrosion in H$_2$S environment: life assessment and methods of preventing

Aleksey Shakhmatov$^{1,*}$, Robert Badrak$^2$, William Howie$^2$, and Sergey Kolesov$^1$

$^1$Weatherford, 195251 Saint Petersburg, Russia
$^2$Weatherford, 11909 Houston, USA

Abstract. Issues of using silver as the braze material in H$_2$S environment are discussed due to environment related sulfidation which cause corrosion penetration and risk of compromising seals. To explore risk and mitigation techniques, static H$_2$S high temperature silver braze corrosion tests were conducted. The results are presented and interpreted by Arrhenius equation approach. The corrosion rate decreased with time due to the formation of Ag$_2$S corrosion product layer. This corrosion product changed the chemical reaction type from mass transfer controlled to diffusion controlled. The environment temperature vs braze joint thickness vs guarantee period relationships are shown and discussed. Additionally, possible protection options connected with metallic and non-metallic coating were investigated.

1 Introduction

The application of silver (Ag) as the braze material relates to sealing connection of materials where other methods to build joints are practically limited. Considering brazes wettability and proving sealing connection with enough strength the corrosion could be a potential operational problem in the field conditions. Using silver as the braze material in H$_2$S environment and its susceptibility sulfidation could cause corrosion penetration and risk of compromising seals. Corrosion study of different configured silver braze samples is presented herein.

2 Experimental

2.1 Material

Corrosion samples were produced by applying silver braze on C-276 substrates. Silver braze material was the pure silver wire that contained 99.99 wt. % Ag. Brazing operation was performed using a manual flame torch technique. The silver brazed samples were tested in the coupled (SC) and not coupled (S) conditions to evaluate the potential galvanic effects between the silver braze and the C-276 substrate. The not-coupled samples were produced by using heat resistant lacquer coating on the C-276 to electrically isolate the braze alloy.

Additionally, we investigated techniques to protect the silver braze from the environment. For this purpose, silver braze samples were epoxy coated (SEC) and gold plated (SGP). Epoxy coating was applied manually and cured. Gold plating protection was applied at via galvanizing operation resulting the gold plating thickness equal to $\approx 5$ µm. External view of prepared corrosion samples is shown in Figure 1.

Fig. 1. Corrosion samples: (S) silver braze with isolated substrate, (SC) silver braze coupled with substrate, (SEC) epoxy coated silver braze, (SGP) gold plated silver braze.

Prior to corrosion tests all samples test surfaces areas were measured by image analyser [1] using light microscopy to characterize any localized corrosion attack and permit corrosion rate calculations from weight loss data. The samples surface areas range was equal to 1.19-2.08 cm$^2$. The one tested had the relatively extreme area value equal to 3.58 cm$^2$ that had an impact on weight loss.

2.2 Procedure

Corrosion tests were performed by immersion test technique according to experimental matrix (Table 1) that was developed with consideration of Arrhenius equation approach [2].
Tests were provided in glass cells where samples were placed on the floor of the cells. Cells heating were provided by electric heaters. Deaeration and subsequent H$_2$S saturation were maintained by 2 hours bubbling through immersed tube with pure nitrogen and H$_2$S gases respectively. Detailed view of samples located in corrosion cells during test is presented in Figure 2. As it was observed during several hours of H$_2$S saturated liquid environment exposure silver brazed samples were covered by dark corrosion products whereas gold plated samples stayed clean (Fig. 2). Corrosion product chemical analysis revealed Ag$_2$S compound.

Table 1. Corrosion test conditions and experimental matrix

| Test conditions: | Static, deaerated, 3.5 wt. % NaCl, H$_2$S saturated pH 3.5-4.0 |
|------------------|-------------------------------------------------------------|
| Days             | Temperature, °C    | S, SC     | S, SC     | S, SC     | S, SC, SEC, SGP |
| 1                | 66                |           |           |           |
| 1                | 88                | S         | S         | S         | S, SC, SEC, SGP |
| 2                | 66                | S         | S         | S         | S, SC, SEC, SGP |
| 10               | 66                | S, SC     | S, SC     | S, SC     | S, SC, SEC, SGP |
| 10               | 77                | S, SC     | S, SC     | S, SC     | S, SC, SEC, SGP |
| 10               | 88                | S, SC     | S, SC     | S, SC     | S, SC, SEC, SGP |
| 20               | 66                | S, SC     | S, SC     | S, SC     | S, SC, SEC, SGP |
| 20               | 77                | S, SC     | S, SC     | S, SC     | S, SC, SEC, SGP |
| 20               | 88                | S, SC     | S, SC     | S, SC     | S, SC, SEC, SGP |

The ±2°C temperature variation of each corrosion cell was observed during tests. Final environment pH measurements results showed following variation 3.67±0.04. It was observed that in non-artificially pressurized corrosion cell (H$_2$S saturated, 1 bar pressure) H$_2$S content decreases with the temperature increasing (Table 2). That fact is in good agreement with theoretical understanding on gas solubility in liquid brine phase as a function of temperature.

3 Test results

3.1 Visual examination

Photographs of the samples as produced and after environment exposure conditions are presented in Figure 3. There were no visual differences between the silver braze samples that were coupled and non-coupled silver. From visual comparison we can conclude that silver tends to react with H$_2$S by forming dark Ag$_2$S corrosion product while gold appeared unaffected. The epoxy coated samples exhibited a color change from dark to light grey from the visual inspection. This change was an indication that the epoxy coating, either by thermal aging or by H$_2$S exposure, was undergoing a change. This change has the potential effect of permitting migration of the environment through the coating to the silver braze resulting in silver sulfidation beneath the coating.

Table 2. pH and H$_2$S content corrosion cells measurements results

| Corrosion cell | Measured parameters in the end of the test |
|----------------|---------------------------------------------|
| Days           | Temperature, °C | H$_2$S content, ppm | pH | final pH |
| 1              | 66                | 1001              | 3.67 |
| 1              | 88                | 579               | 3.68 |
| 2              | 66                | 1159              | 3.71 |
| 2              | 88                | 567               | 3.62 |
| 10             | 66                | 990               | 3.69 |
| 10             | 77                | 760               | 3.72 |
| 10             | 88                | 569               | 3.72 |
| 20             | 66                | 1012              | 3.63 |
| 20             | 77                | 849               | 3.62 |
| 20             | 88                | 653               | 3.66 |

The silver braze sulfidation under the epoxy coating was confirmed in several samples due to coating delamination during the process of removing the test samples from the corrosion cell (Fig. 4). This delamination also affected the weight loss data.

Fig. 2. Detailed view of corrosion cell and samples placement

Fig. 3. Examples of before and after H$_2$S corrosion tests samples views.

Fig. 4. Examples of before and after H$_2$S corrosion tests samples views.
Visual examination of the gold plated silver brazed samples after weight scale measurements and following careful light grinding by abrasive paper to remove just the gold layer did not reveal any corrosion damage on the silver braze (Fig. 4).

### 3.2 Weight loss corrosion rates

Weight loss measurements were performed with ±0.0001 g scale accuracy. Samples were weight after corrosion product removal. Corrosion product removal procedure was included by 5 steps: (1) water flush, (2) brush cleaning, (3) rubber cleaning, (4) acetone and ethanol degreasing and (5) drying. Weight loss corrosion rates data is presented in Table 3.

![Table 3. Weight loss measurements results](image)

From the data in Table 3 only the silver brazed and the silver brazed and coupled samples exhibited significant weight loss. The very minor weight losses observed on gold plated samples are close to the measurement accuracy; this corresponds to the inert nature of gold in the H₂S test environment and the resultant protection of the underlying silver braze (Fig. 4). The large weight loss variations observed on the epoxy samples were due to the delamination details that were discussed earlier (Fig. 4).

The silver braze and silver brazed and coupled weight loss data were used to calculate corrosion rates in order to obtain the relationship versus temperature and test duration. Corrosion rates were calculated according to ASTM G31 [3].

![Fig. 5. Evolution of silver braze (S – not coupled with substrate, SC – coupled with substrate) corrosion rates in H₂S environments during test periods.](image)

Corrosion rates of silver braze in H₂S environment decreases with test period duration increasing (Fig. 5) which is related to Ag₂S protective corrosion product layer formation. This corrosion product changed the chemical reaction type from mass transfer controlled to diffusion controlled. Also, the increased temperature results to observation of relatively high increased corrosion rates in first test periods. That fact could relate to corrosion product layer thickness and its positive dependence on temperature [4]. It should be mentioned that there was no big difference observed between silver braze and silver braze coupled with C-276 samples on corrosion rates. So, there is no experimental evidence on galvanic effect on this process.

### 3.3 Data interpretation

The obtained silver braze 20 days steady state corrosion rates data at different temperatures were analyzed in order to obtain Arrhenius relationship equation. The following rates (Fig. 5) were taking into account for equations investigations: 0.24, 0.41, 0.53 mmpy (mm/year) for S samples and 0.19, 0.32, 0.41 mmpy for SC samples at 66, 77, 88 °C environment temperatures, relatively. It was possible to evaluate corrosion rate constant and activation energy by building linear extrapolation in coordinates ln (r) and 1/T where ln (r) – natural logarithm of 20 days corrosion rate in mmpy and 1/T – relative temperature in K⁻¹. The obtained linear extrapolations and relative equations are shown below on Figure 6.

![Fig. 6. The results of ln(r) vs 1/T plotted in order obtain the gradient and intercept of silver braze not coupled samples (grey line) and silver braze coupled samples (dark line) Arrhenius equation](image)

Due to no galvanic influence the obtained equation for silver braze sulfidation (Fig. 6, S samples) permits calculations to estimate time to failure in silver brazed braze joints under static conditions in contact with high H₂S content production environments. Plots where time (in years) that needed for sulfidation through end-to-end
different thicknesses of braze joints versus temperature are presented in Figure 7.

![Figure 7: Time to sulfidation related failure of silver braze depending on temperature and joint thickness.](image)

According to Fig. 7, the significant life assessment decreasing with environment temperature increasing is expected. The root cause of this is silver sulfidation reaction kinetic increasing.

### 4 Discussion and Conclusions

The corrosion study presented results that showed that the resultant Ag₂S products effect on reaction rate kinetics by protective layer formation under static condition. This layer could have dynamic adhesion properties to base substrate which tends to decrease over time. This also suggests that a disturbance or damage to the sulfide layer could result in old (or initial) layer of Ag₂S removal or bonding that results in new layer formation. As it was shown and based on 1- and 2-days immersion data increased corrosion rates were observed at the beginning of exposure.

So, system conditions like flow and vibrations could have a strongly effect on corrosion rates due to increases in new sulfide film formation. The worst situation would be for a continual removal of the corrosion product that results in the highest corrosion rate. In this worst-case scenario, the corrosion rate could remain at the highest initial level. As a function of temperature, this corrosion rate could range from 4 - 8 mm/year and this results in a silver braze service life that on the order of one year. In the scenario of adherent corrosion products formation and its growth the 10 year service life could be guaranteed for 10 mm braze joint and environment temperatures below 100°C (Fig. 7).

The epoxy coating as a possible solution slows the process but, in our experiment, it did not positively stop the silver braze sulfidation reaction. Epoxy could add environment barrier, but it is penetrable for H₂S molecules. As it was discovered with silver braze samples sulfidation reaction started to be diffusion controlled as acceptable products layer forms under static condition. In case of epoxy coating silver braze sulfidation could be described as mass transfer controlled chemical reaction in first period of immersion. From the test results reported here, we were unable to predict the period in which epoxy works as mass transfer barrier for environment. Such processes like thermal or chemical aging that are commonly known for non-metallies material could affect on epoxy performance. Also, the formation of corrosion products under the epoxy could promote delamination. One method to increase the reliability of an epoxy protective coating could be preparing a roughened silver braze surface that would result in greater coating adherence.

The most effective way to protect the silver braze from sulfidation investigated here was gold plating. There was no significant weight loss/gain on the gold plated corrosion samples. A thickness of about 5µm was found to be sufficient for protection. The main benefit of gold plating as the protection method is that it doesn’t give a chance to sulfidation reaction to occur. The primary reason for the success of gold with respect to sulfidation is that the gold sulfidation reaction has a high positive ∆G value [5]. A positive ∆G means that sulfidation does not naturally occur with gold and energy must be spent to cause the reaction.

### References

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