1. Introduction

Copper pipes are mostly used for the distribution of gas and liquid media in a variety of industries. They are used for their excellent corrosion properties and long life [1 - 6]. Due to the differences in device geometry of distribution lines, copper pipes must be bent in certain locations or linked with another circuit. At present mainly three types of joints are used to connect copper pipes. They are the permanent joints made by soft or hard soldering and the demountable joints formed by pressing plastic ring which creates a joint between the copper pipes fixed closed connection (the fitting) [7 and 8]. The joints in copper pipes comprise inhomogeneities which affect, e.g. media flow change, character and sedimentation of corrosion products and thus the degradation process. The main aim of the work was to monitor the synergetic effect of mechanical and chemical stress on corrosion-erosion behavior of the copper pipes joints. The degradation was assessed visually, by light and scanning electron microscopy.

2. Experiments

Corrosion behavior of the copper pipes joints was verified by a long-term experiment lasting 11 months. The experimental conditions were chosen to simulate the ones in real distribution. During a day boundary conditions by increasing the temperature and flow of the working medium were set because even their short-term activity can influence the course of corrosion processes.

2.1 Equipment and conditions

For the experiment two identical devices of technical copper (99.5% ± 0.5% Cu) with two types of permanent joints (soft and hard soldering) and one type of demountable molded joint were made. In Fig. 1 the experimental equipment with the marked localities of joints is shown. Joints were formed under the following conditions:

1. Soft soldering (Fig. 1, area 2, 5, 11) was performed according to DIN 1707 solder L-SnCu3 (DIN EN 29453, S-Sn97Cu3) at 230°C.
2. Hard soldering (Fig. 1, area 4, 6) was performed according to DIN 8513 (EN 1044) using flux and solder CP 203 and L-CuP6 at 730°C.
3. The demountable fitting was created by pressing of Cu pipes with the polymers (Fig. 1, area 3, 9).

Experimental conditions were chosen to simulate operating conditions in practice. The first experimental equipment was filled with the 3% sodium chlorid solution, 16 hours exposed at 20 ± 2 °C without flow of the solution, 8 hours at 80° C per day. In one of the devices for 8 hours the experimental solution was flowing by the input speed 0.27m.s⁻¹. In the second one no flow was applied. Evaluation of the joints corrosion attacks was performed visually, by light and scanning electron microscopy.

Keywords: Copper pipes, joints, corrosion, corrosion products.
3. Results

After 11 months of exposure the samples were taken off, incised to be possible to assess corrosion attack of the monitored joints in stagnant and flow conditions. Assessment of the different joints after exposure was made visually, by light and scan electron microscopy.

3.2 Hard soldering joints

Corrosion attack in the localities of the joint is the same as the one of Cu pipes. In stagnant conditions the corrosion products were black-grey. According to the Pourbaix diagram corrosion products in aqua environment are (in the potential range from -0.15V to +0.521V) formed by CuO (Cu²⁺) which are black and complex compounds CuCl₁₃Cu(OH)₂. Higher temperature (80°C) does not influence the character of corrosion products but their formation is shifted to more acid area (lower value of pH). When the solution is flowing, the character of corrosion products is changed by hydrolysis to greenish color (presence of CuCl and CuCl⁺⁺) as shown in Fig. 2. These corrosion products have pure adherence and by flow they are torn off from the metal surface especially on the top of the pipe. No differences of corrosion product character between Cu pipe and the locality of hard soldering joints are observed. In Fig. 2b, the start of intergranular corrosion on the joint and Cu pipe boundary was observed. In flow conditions the surface roughness
of the soldering joint and corrosion attack in flow and no flow conditions is shown in Fig. 3a. The Sn solder has quite good corrosion resistance. In corrosion environment (scale pH 3.5 - 9) the stable oxides SnO and SnO₂ are created on the surface and feature protection character. The Sn solder creates with Cu pipe a local galvanic sell in the electrolyte and Sn behaves as an anode. After the experiment the local corrosion was determined in the Sn joints in stagnant and flowing conditions. Local corrosion was evoked by of the joint can change the flow character and increase its effect on damage of Cu pipe system by corrosion-erosion (Fig. 2a, 6A).

3.3 Soft soldering joints

The joints created by soft soldering differ from Cu pipe by chemical composition of solder (97% tin Sn). Metallography of the soldering joint and corrosion attack in flow and no flow conditions is shown in Fig. 3a.

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In Table 1 chemical composition of corrosion products in stagnant and flow conditions is specified.

<table>
<thead>
<tr>
<th>Element</th>
<th>Stagnant conditions</th>
<th>Flow conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight %</td>
<td>Atom. %</td>
</tr>
<tr>
<td>O</td>
<td>8.7</td>
<td>31.65</td>
</tr>
<tr>
<td>Cl</td>
<td>0.56</td>
<td>0.91</td>
</tr>
<tr>
<td>Cu</td>
<td>57.67</td>
<td>49.85</td>
</tr>
<tr>
<td>Sn</td>
<td>36.03</td>
<td>17.59</td>
</tr>
</tbody>
</table>

Intensive corrosion of Sn solder was confirmed by EDX analysis of its corrosion products. The Sn corrosion products diffuse to the electrolyte and they are accumulated in the bottom of Cu pipe. In Fig. 5 the character of corrosion products made by SEM near Sn joint can be seen (a) and a map of Sn distribution (light points) in stagnant solution (b). In Fig. 6 the character of corrosion products is compared with Sn distribution from identical place but in flowing solution. Sn corrosion products are more scattered by flow influence and mixed with Cu corrosion products. It is proved by the EDX analysis of corrosion products in no flowing and flowing conditions in the identical places.
erosion impact is the main cause of faster damage of copper in flow environment. • Tin joints are attacked by pitting corrosion in medium containing chlorides. The intensity of corrosion damage is not very dangerous for actual dimensions of joint and their stability is not endangered. The empty places originated by inappropriate soldering are more dangerous for safety of the joint. The solid particles of the Sn corrosion products increase the erosion effect in flow conditions. • Demountable joints formed by pressing plastic rings with polymer material tighten excellently even in aggressive 3% NaCl solution in stagnant and flowing conditions too. The joints create only a little mechanical barrier for flowing medium in Cu pipe system. The hidden areas in the joint locality were in untouched state without any sign of corrosion or in-leak between joined pipes.

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3.4 Fitting

The demountable joint - fitting was constructed at normal room temperature by pressing of Cu pipes with polymer. In this way a very good sealing joint was created without any intermediate film. As it can be seen in Fig. 7a, fitting did not affect character of the Cu corrosion products in stagnant and flow conditions. In the joint locality of Cu pipes no corrosion attack was observed. In moving solution only joint protrusions can slightly change the linear flow. In Fig. 7b the character and intensity of Cu pipe corrosion in stagnant (B) and flow conditions (A) are presented.

4. Conclusions

With regard on the obtained results share can be stated:

Conclusions
• Joints molded by hard soldering were not attacked more intensively than basic material - technical copper. The joint forms in the pipe system crevices and stagnation of operating medium in these crevices creates conditions for corrosion attack. Geometry of crevices can also cause changes in lamellar flowing of operating solution and so it can increase its mechanical effect. The loss of stability of protective cuprous oxide layer due to the hydrolysis and corrosion-erosion impact is the main cause of faster damage of copper in flow environment.
• Tin joints are attacked by pitting corrosion in medium containing chlorides. The intensity of corrosion damage is not very dangerous for actual dimensions of joint and their stability is not endangered. The empty places originated by inappropriate soldering are more dangerous for safety of the joint. The solid particles of the Sn corrosion products increase the erosion effect in flow conditions.
• Demountable joints formed by pressing plastic rings with polymer material tighten excellently even in aggressive 3% NaCl solution in stagnant and flowing conditions too. The joints create only a little mechanical barrier for flowing medium in Cu pipe system. The hidden areas in the joint locality were in untouched state without any sign of corrosion or in-leak between joined pipes.

Fig. 7 Localities of fitting in stagnant 9B and flow conditions 9A a) and microstructure of corrosion attack (b)
References


