

# CHEMICAL CLEANING OF SOLIDIFIED LEAD FROM 316 AUSTENITIC STEEL A STRUCTURE CANDIDATE MATERIAL FOR LEAD-COOLED FAST REACTORS

## CURATAREA CHIMICĂ A PLUMBULUI SOLIDIFICAT DE PE OȚELUL AUSTENITIC 316 CANDIDAT PENTRU REACTORII RAPIZI RĂCIȚI CU PLUMB

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**Abstract:** *The aim of this study is to find a specific cleaning solution that removes solidified lead from a candidate material for Lead-cooled Fast Reactors (LFR) without damaging it.*

*Among the promising reactor technologies being considered by the Generation IV International Forum (GIF), the Lead-cooled Fast Reactor has been identified as a technology with great potential, because this system can fulfill simultaneous several key objectives like sustainability, non-proliferation, economics and safety. Some of these goals are achieved thanks to the favourable inherent properties of lead. With his very high boiling point, low vapour pressure, high shielding capability, high heat transfer, high density, small neutron absorption cross-section, good compatibility with air and water, lead permits to extend the viability domain for reactor design, opening new possibilities for a greatly simplified system configuration.*

*In service inspection and repair (ISIR) is an important issue in the development of the next generation nuclear systems as it contributes greatly to the safety of the system. For the inspection of components removed from the reactor vessel, it is very important to be able to clean the structural material from residual lead without damaging it. Therefore, in this paper, several chemical cleaning solutions were studied. In order to remove residual lead from the surface of candidate materials for LFR, first were tested 316 stainless steel specimens in liquid lead at 450 °C for 48 hours.*

*Among the tested solutions that proved their efficiency for lead removal were several mixtures based on acetic acid, hydrogen peroxide, and alcohol (ethanol and propanol). All of these were tested under two temperature conditions: 20 °C and 75 °C. The cleaning speed was significantly faster for the mixtures that had a higher temperature. Other solutions that were totally ineffective or had affected the austenitic steel and the protective oxide layer are nitric acid, aqua regia and the electrolytic solution of fluoboric acid.*

*A series of analyses were performed on all austenitic steel specimens after each immersion period in the cleaning solutions: microscopic, gravimetric and Vickers microhardness. These analyses showed that the solutions based on organic acids were more appropriate for removing residual lead from the 316 austenitic steels.*

**Keywords:** lead-cooled fast reactor, chemical cleaning, austenitic steel

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**Rezumat:** Scopul lucrării este acela de a identifica o soluție de curățare specifică pentru înlăturarea plumbului solidificat de pe un material candidat pentru Reactorii Rapizi raciti cu Plumb (LFR) fara deteriorarea acestuia.

Printre tehnologiile promitatoare de reactoare care au fost luate in considerare de Forumul International de Generatie IV (GIF), LFR a fost identificat ca o tehnologie cu un mare potential, deoarece acest sistem poate indeplini simultan mai multe obiective cheie, cum ar fi durabilitatea, neproliferarea, economia si siguranta. Unele dintre aceste obiective sunt realizate datorita proprietatilor inerente favorabile ale plumbului. Cu punctul de fierbere foarte ridicat, presiunea scazuta a vaporilor, capacitatea de ecranare ridicata, transferul de caldura ridicat, densitatea mare, sectiune scazuta de absorbtie a neutronilor si compatibilitatea buna cu aerul si apa, face ca plumbul sa extinda domeniul viabilitatii pentru proiectarea reactorului, pentru o configurație a sistemului foarte simplificata.

Inspectia si reparatia sunt niste probleme importante pentru dezvoltarea sistemelor nucleare de generatie noua, deoarece contribuie in mare masura la siguranta intregului sistem. Pentru inspectia componentelor scoase din vasul reactorului este foarte important sa se poata curata materialul structural de plumbul rezidual fara ca acesta sa fie afectat. Prin urmare, in aceasta lucrare au fost studiate cateva solutii chimice de curățare. Pentru a indeparta plumbul rezidual de pe suprafata materialelor candidate pentru reactoarele LFR, s-au testat mai intai probe de otel inoxidabil 316 in plumb lichid la 450 °C timp de 48 de ore.

Dintre solutiile testate care si-au dovedit eficienta pentru înlăturarea plumbului au fost cateva amestecuri pe baza de acid acetic, apa oxigenata si alcool (etanol si propanol). Toate acestea au fost testate in doua conditii de temperatura: 20 °C si 75 °C. Viteza de curățare a fost semnificativ mai rapida pentru amestecurile care au avut temperatura mai mare. Alte solutii care au fost testate, dar s-au dovedit a fi total ineficiente sau au afectat otelul austenitic si stratul oxidic protector sunt acidul azotic, apa regala si solutia electrolitica de acid tetrafluoroboric.

S-au efectuat o serie de analize pe toate probele de otel austenitic dupa fiecare perioada de imersie in solutiile de curățare chimica: microscopice, gravimetrice si microduritate Vickers. Analizele au aratat ca amestecurile de solutii cu acizi organici au fost mai potrivite pentru indepartarea plumbului de pe otelurile austenitice 316.

**Cuvinte cheie:** reactor rapid racit cu plumb, curățare chimica, otel austenitic

## 1. Introduction

High-level radioactive waste disposal is an issue of great importance in the discussion of the sustainability of nuclear power generation. The main contributors to the high radioactivity are the fission products and the minor actinides. The long-lived fission products and minor actinides set severe demands on the arrangements for safe waste disposal [1].

Lead-cooled Fast Reactors (LFRs) and Accelerator Driven Systems (ADS) are studied in Member States to reduce the long-term hazard of spent fuel and

radioactive waste, taking advantage of their incineration and transmutation capability. The conceptual design of lead/lead-bismuth cooled fast reactors have been developed to meet enhanced safety and non-proliferation requirements, aiming at both energy production and transmutation of nuclear waste. Some R&D studies indicate that the use of lead and lead-bismuth coolant has some advantages in comparison with existing sodium-cooled fast reactor systems, e.g.: simplified design of fast reactor core, enhanced inherent safety, and easier radwaste management in related fuel cycles [2].

In Figure 1 are presented the conceptual designs for MYRRHA (Multi-purpose hybrid Research Reactor for High-tech Applications), an accelerator driven system developed by SCK-CEN, Belgium, which uses lead-bismuth eutectic (LBE) as coolant, and ALFRED (Advanced Lead-cooled Fast Reactor European Demonstrator) designed by FALCON consortium and planned to be built in Mioveni, Romania.

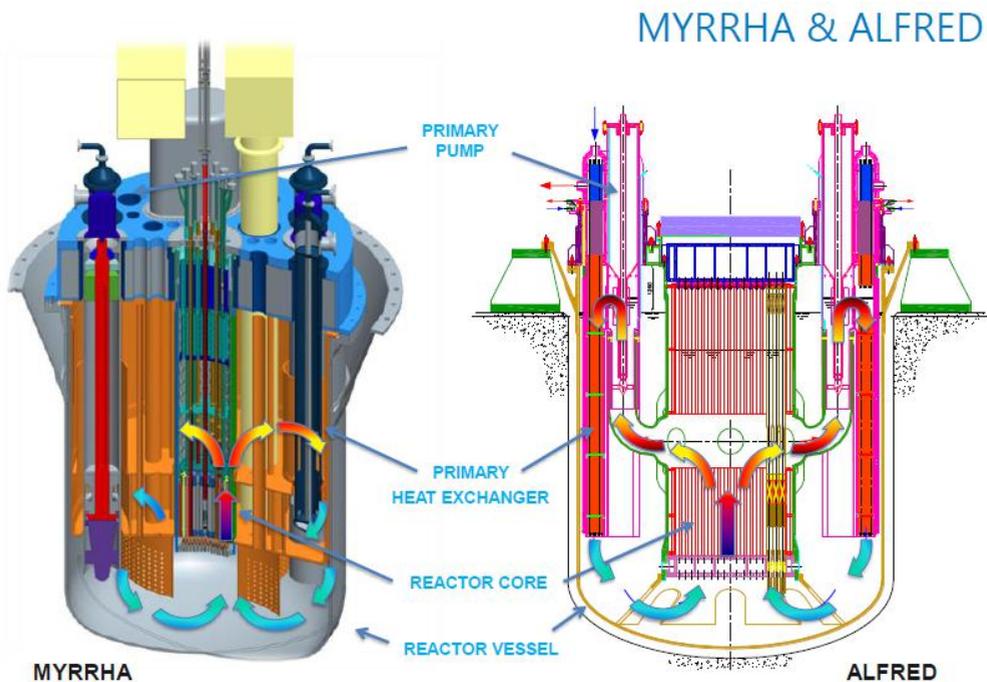


Figure 1. MYRRHA and ALFRED system designs [3]

The main features of these two reactor concepts, which are cooled with heavy metals, are presented in table 1.

Table 1. Main characteristics for MYRRHA and ALFRED reactors [3]

|                               | MYRRHA v1.6                                | ALFRED                                 |
|-------------------------------|--|--|
| Thermal power                 | 100 MWth                                   | 300 MWth                               |
| Primary coolant               | Lead Bismuth Eutectic                      | Lead                                   |
| Primary circulation           |  |  |
| Normal operation              | Forced (2 mechanical pumps)                | Forced (8 mechanical pumps)            |
| Accident conditions           | Natural                                    | Natural                                |
| Primary system temperature    | 270 ÷ 325 °C                               | 400 ÷ 480 °C                           |
| Primary system flow rate      | 13800 kg/s                                 | 26000 kg/s                             |
| Secondary system coolant      | Water/Steam                                | Water/Superheated-Steam                |
| Secondary system pressure     | 1,6 MPa                                    | 18 MPa                                 |
| Secondary system temperature  | 200 °C                                     | 450 °C                                 |
| Residual heat removal systems | DHR system, 4 independant loops<br>Passive | 2 DHR systems, 4 loops each<br>Passive |
| Vessel diameter               | 10,4 m                                     | 8 m                                    |
| Vessel height                 | 12,56 m                                    | 10,13 m                                |

## 2. Experimental

For the inspection of components removed from the reactor vessel, it is very important to be able to clean the structural material from residual lead without damaging it. Therefore, in this paper, several chemical cleaning solutions were studied. In order to remove residual lead from the surface of candidate materials for Lead-cooled Fast Reactors, first were tested 316 stainless steel specimens in liquid lead at 450 °C for 48 hours. The visual aspect of specimens, before and after testing in liquid lead, it is presented in Figure 2.

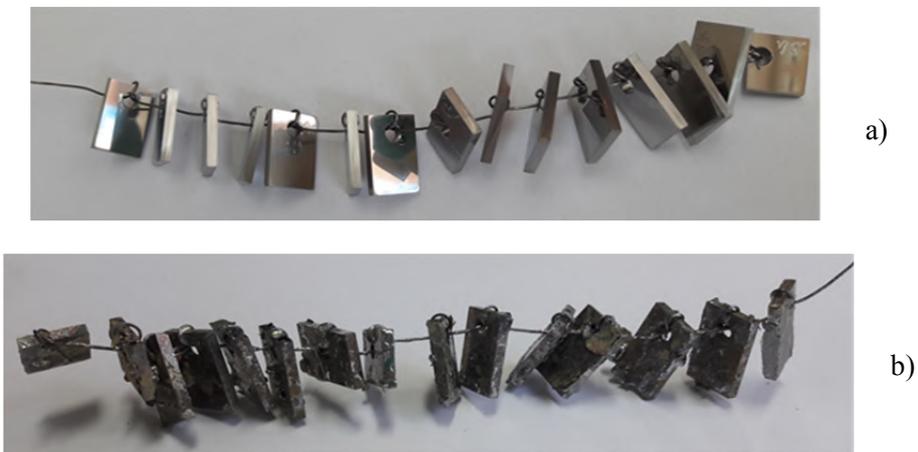


Figure 2. 316 stainless steel specimens a) before testing in liquid lead b) after testing in liquid lead

After 48 hours of immersion in liquid lead, all the austenitic steel samples were cooled in air and then sent to analytical balance to see the weight gain. Forwards, several organic and inorganic mixtures were prepared in order to remove solidified lead from the specimens. Table 2 presents the tested solutions for each specimen in different temperature conditions.

Table 2. Solutions tested in different condition for lead removing from the specimens

| Solution                                   | Testing condition | Specimen number |
|--|-------------------|-----------------|
| Hydrogen peroxide + acetic acid            | 20 °C             | 4               |
| Hydrogen peroxide + acetic acid + propanol | 20 °C             | 3               |
| Hydrogen peroxide + acetic acid + ethanol  | 20 °C             | 5               |
| Hydrogen peroxide + acetic acid            | 75 °C             | 2               |
| Hydrogen peroxide + acetic acid + propanol | 75 °C             | 7               |
| Hydrogen peroxide + acetic acid + ethanol  | 75 °C             | 9               |
| Azotic acid                                | 75 °C             | 1               |
| Aqua regia                                 | 75 °C             | 8               |
| Fluoboric acid                             | 20 °C, 10 V       | 11              |

### 3. Results and discussion

The mixture of hydrogen peroxide and acetic acid (Sol.1) was tested at 20 °C on specimen 4 and at 75 °C on specimen 2. Figures 3 and 4 present some visual aspects of specimens 4 and 2 before and after the cleaning test.

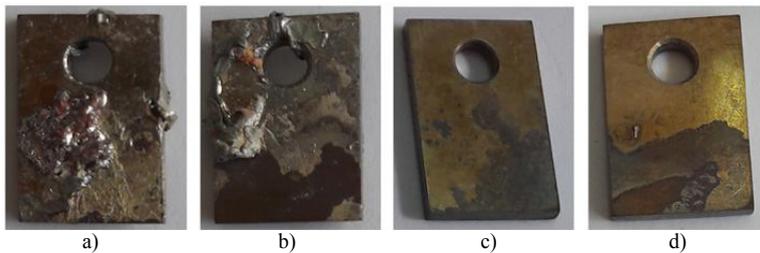


Figure 3. Specimen 4 a), b) front-back before cleaning test c), d) front-back after cleaning test for 15 minutes in Sol.1 at 20 °C

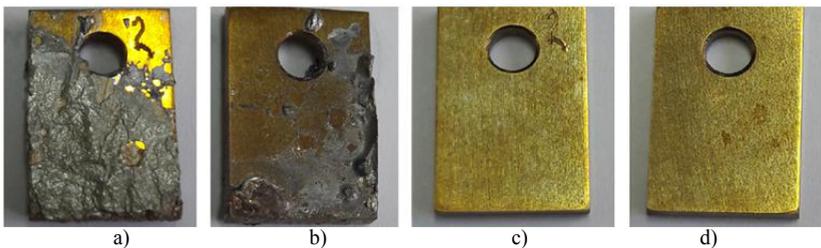


Figure 4. Specimen 2 a), b) front-back before cleaning test c), d) front-back after cleaning test for 3 minutes in Sol.1 at 75 °C

Almost 99,85% of residual lead was removed from the sample 4 after 15 minutes of immersion in Sol. 1 at 20 °C and more than 99,99 % of lead from the sample 2 after only 3 minutes of sinking in the same solution but at 75 °C.

A solution made with hydrogen peroxide, acetic acid, and propanol (Sol.2) was tested at 20°C on specimen 3 and at 75 °C on specimen 7. The visual aspects of the samples, before and after cleaning, are presented in Figure 5 and Figure 6.

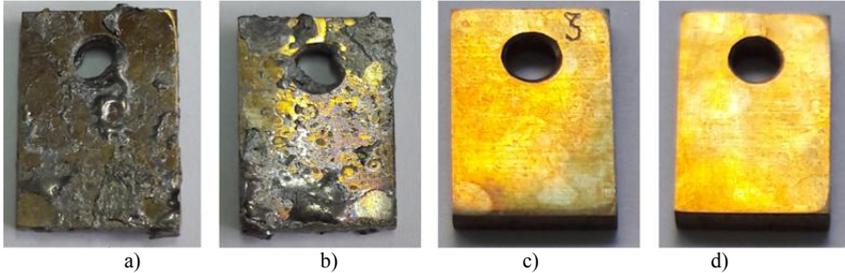


Figure 5. Specimen 3 a), b) front-back before cleaning test c), d) front-back after cleaning test for 15 minutes in Sol.2 at 20 °C

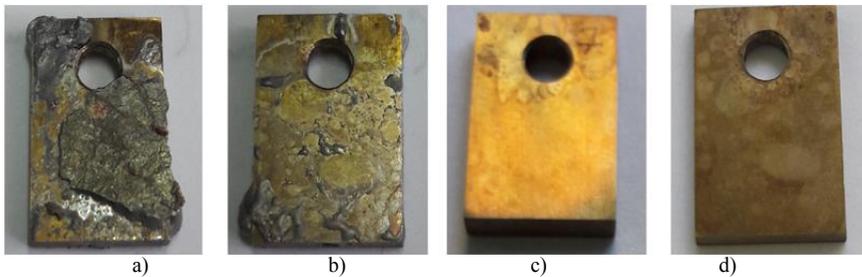


Figure 6. Specimen 7 a), b) front-back before cleaning test c), d) front-back after cleaning test for 1 minute in Sol.2 at 75 °C

Specimen 3 had lost ~83,78 % of the lead after about 5 minutes of immersion in Sol 2 at 20°C and almost ~99,99 % after another 10 minutes of immersion. The percentage of residual lead removed in the case of specimen 7, tested in the same solution but at 75 °C, was about 99,95 % after only 1 minute of immersion. The bright orange color that can be seen in figures 5 c), d) and 6 c), d) is a thin protective oxide layer formed on the surface of the specimens after testing in liquid lead. This film was not affected by the cleaning solution.

Another solution that was tested at 20 °C on specimen 5 and at 75 °C on specimen 9 was obtained by mixing hydrogen peroxide, acetic acid, and ethanol (Sol. 3). In Figures 7 and 8 are presented the visual aspects of these specimens after the cleaning tests for lead removal with Sol. 3.

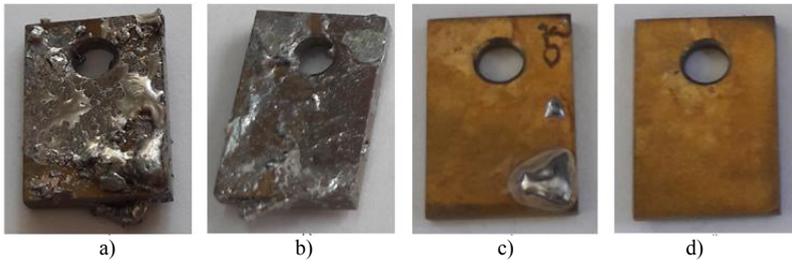


Figure 7. Specimen 5 a), b) front-back before cleaning test c), d) front-back after cleaning test for 15 minutes in Sol.3 at 20 °C

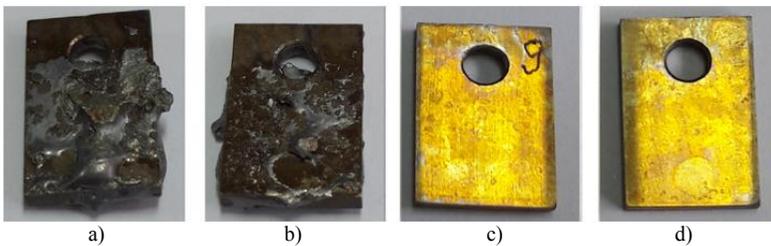


Figure 8. Specimen 9 a), b) front-back before cleaning test c), d) front-back after cleaning test for 3 minutes in Sol.3 at 75 °C

Almost 85,81% of residual lead was removed from specimen 5 after 15 minutes of immersion in Sol. 3 at 20 °C and about 99,97 % of lead was dissolved from specimen 9 after only 90 seconds of sinking in the same solution but at 75 °C. After another 90 seconds of immersion at 75 °C, the percentage of lead removed from specimen 9 was about 99,99 %.

Specimens 5 and 9 presented large drops of solidified lead on their surface. In this case, the lead was not distributed uniformly and the contact surface area with the cleaning solution was reduced, which resulted in an increase of dissolution time.

A separate series of solutions that were tested for lead removal contained inorganic acids. Thus, sample 1 was kept in a nitric acid solution (Sol.4) and its visual aspects, before and after immersion, are shown in Figure 9.

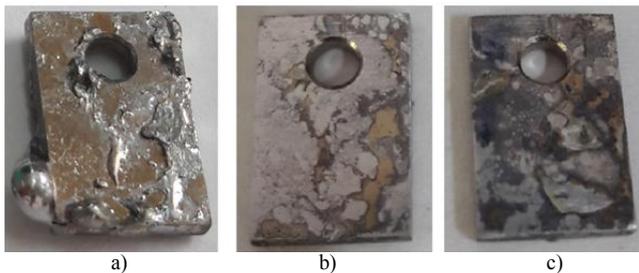


Figure 9. Specimen 1 a) before cleaning test b), c) front-back after cleaning test for 15 minutes in Sol.4 at 75 °C

Specimen 1 was immersed in nitric acid at 75 °C for about 15 minutes. After that, it had lost theoretically 96.07% of solidified lead. As the sample does not look good visually (see Figure 9 b), c)), the mass loss may have occurred from the base material. Also, the protective oxide layer formed on the material surface was affected.

Aqua regia (Sol.5) was another cleaning solution which was tested at 75 °C for lead dissolving. The visual aspects of specimen 8 covered with lead and after the cleaning procedure in Sol.5 are shown in Figure 10.

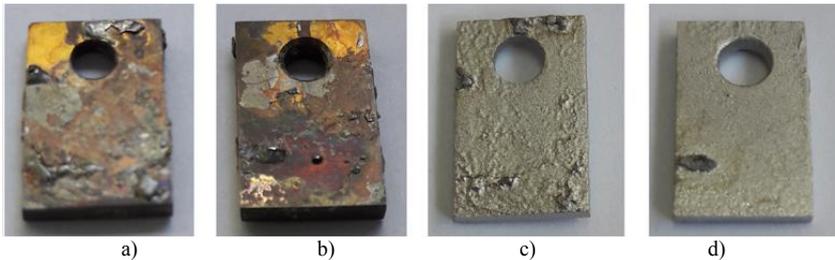


Figure 10. Specimen 8 a), b) front-back before cleaning test c), d) front-back after cleaning test for 5 minutes in Sol.5 at 75 °C

After 5 minutes of immersion in aqua regia at 75 °C, sample 8 underwent a significant degradation. Sol. 5 dissolved both lead and 316 austenitic stainless steel. The degradation of the base material was so strong that it lost 0.5669 grams from its initial weight of 2.0463 grams. The protective oxide film was also destroyed.

The last solution tested for lead removal was fluoboric acid (Sol. 6). The cleaning method involved the electrodeposition of solid lead from the anode on a copper cathode using an electrolytic solution ( $\text{HBF}_4$ ) at a potential of 10 V. Specimen 11 was tested by this method and the visual aspects before and after cleaning are shown in Figure 11.

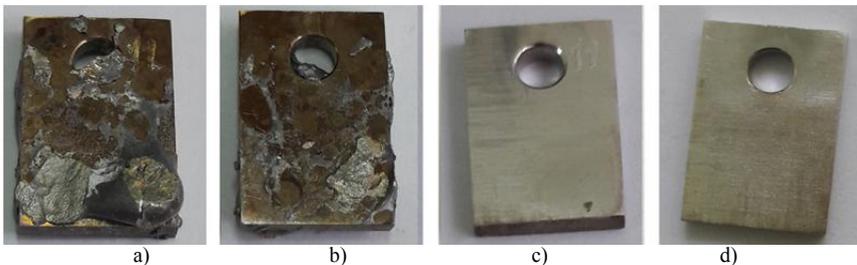


Figure 11. Specimen 11 a), b) front-back before cleaning test c), d) front-back after cleaning test for 5 minutes in Sol.6 at 10 V

As can be seen in Figure 11 c) and d), the solidified lead from sample 11 was removed. However, according to gravimetric analysis, the austenitic steel

suffered a slight weight loss, and the protective oxide film was removed. It is possible that the 10 V potential has been a little too high and thus has affected the oxide layer.

Micrographs of specimens 4 and 2, before and after cleaning test in Sol. 1, are presented in Figures 12 (A, B) and 13 (A, B). These pictures show that solidified lead was successfully removed from specimen surfaces. The micro-indentations for Vickers hardness calculation, which were made in cross-sections of the samples, near the protective oxide layer, are shown in Figure 12 (C) for sample 4 and in Figure 13 (C) for sample 2. The mean microhardness value for specimen 4 was 183 Kgf/mm<sup>2</sup> and for specimen 2 was 189 Kgf/mm<sup>2</sup>.

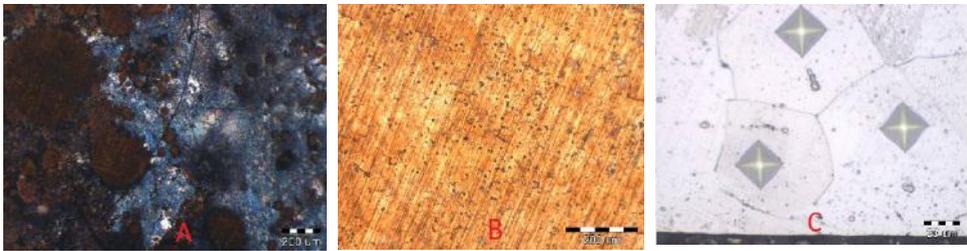


Figure 12. Specimen 4 A) covered with lead B) after cleaning test at 20 °C in Sol. 1 C) Vickers microhardness after cleaning test

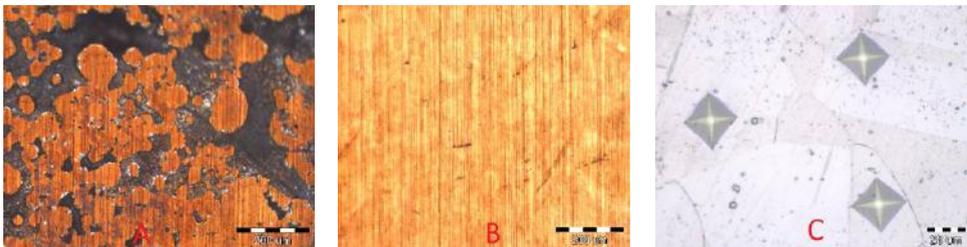


Figure 13. Specimen 2 A) covered with lead B) after cleaning test at 75 °C in Sol. 1 C) Vickers microhardness after cleaning test

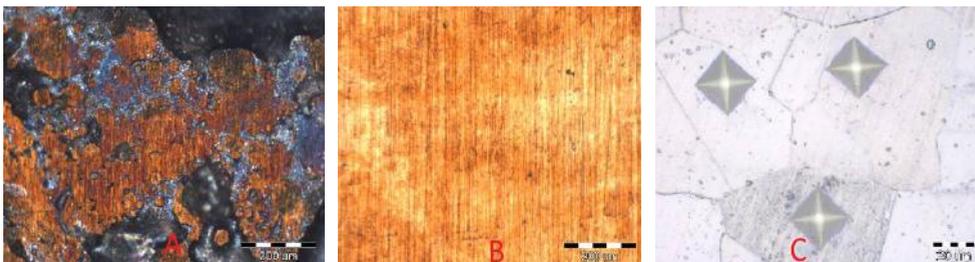


Figure 14. Specimen 3 A) covered with lead B) after cleaning test at 20 °C in Sol. 2 C) Vickers microhardness after cleaning test

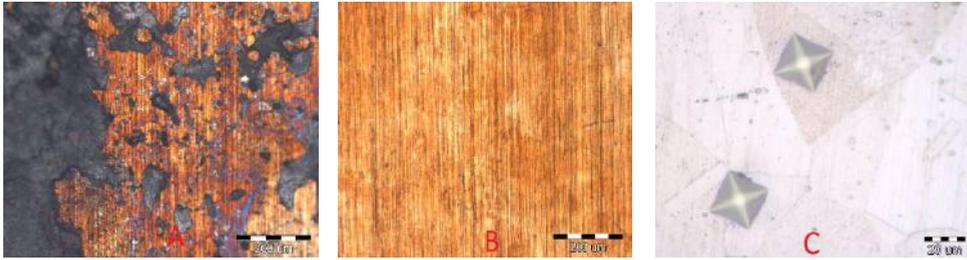


Figure 15. Specimen 7 A) covered with lead B) after cleaning test at 75 °C in Sol. 2 C) Vickers microhardness after cleaning test

Figures 14 (A, B) and 15 (A, B) presents some micrographs of specimens 3 and 7 before and after cleaning test in Sol. 2. These pictures show that Sol. 2 was also efficient for lead removal from the surface of both samples. Microhardness measurements showed values of 183 Kgf/mm<sup>2</sup> for sample 3 and 187 Kgf/mm<sup>2</sup> for sample 7.

As can be seen in Figures 16 (A, B) and 17 (A, B), Sol. 3 removed almost all the lead from the samples without affecting the protective oxide layer from the stainless steel. The Vickers microhardness for specimens 5 and 9 was 181 Kgf/mm<sup>2</sup> respectively 186 Kgf/mm<sup>2</sup>.

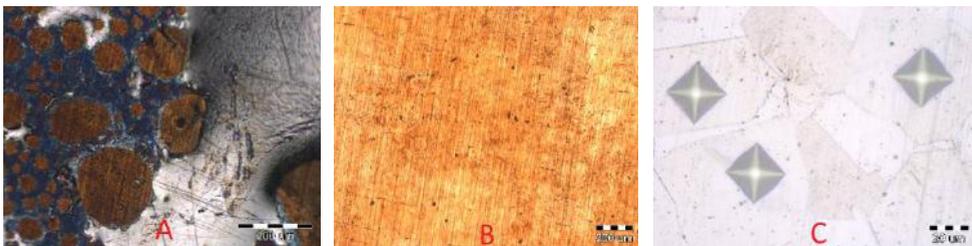


Figure 16. Specimen 5 A) covered with lead B) after cleaning test at 20 °C in Sol. 3 C) Vickers microhardness after cleaning test



Figure 17. Specimen 9 A) covered with lead B) after cleaning test at 75 °C in Sol. 3 C) Vickers microhardness after cleaning test

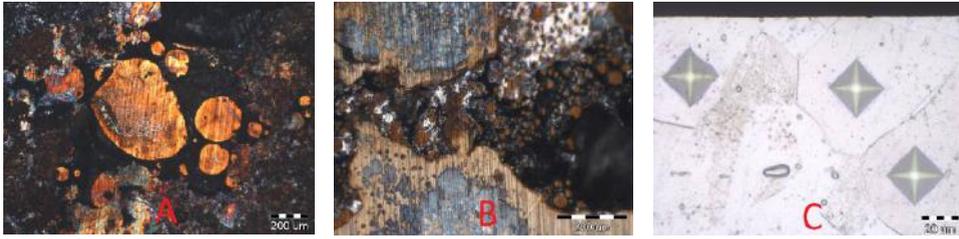


Figure 18. Specimen 1 A) covered with lead B) after cleaning test at 75 °C in Sol. 4 C) Vickers microhardness after cleaning test

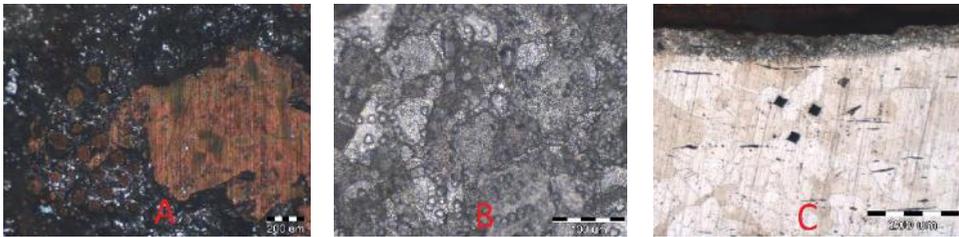


Figure 19. Specimen 8 A) covered with lead B) after cleaning test at 75 °C in Sol. 5 C) Vickers microhardness after cleaning test

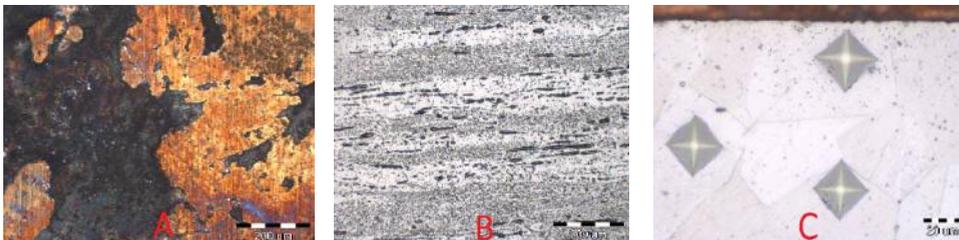


Figure 20. Specimen 11 A) covered with lead B) after cleaning test at 10 V in Sol. 6 C) Vickers microhardness after cleaning test

As seen in the micrographs of Figures 18, 19 and 20, solution 4 failed to remove the lead from sample 1, solution 5 dissolved both the lead and the base material of sample 8, and solution 6 removed the lead but also the protective oxide layer from sample 11. The calculated microhardness values were 186 Kgf/mm<sup>2</sup> for specimen 1, 189 Kgf/mm<sup>2</sup> for specimen 8 and 184 Kgf/mm<sup>2</sup> for specimen 11.

#### 4. Conclusions

- After testing 316 austenitic steel in liquid lead for 48 hours, a protective oxide layer was formed on its surface;
- Chemical solutions based on hydrogen peroxide, acetic acid, and alcohol (ethanol/propanol) were able to remove almost completely the lead from the specimens without affecting the protective oxide layer or the steel structure;

➤ The speed for lead removal from the samples was significantly influenced by the temperature. Thus, the same solutions that cleaned the lead from the samples within 15 minutes at 20 °C were able to remove the lead in just 1-3 minutes at 75 °C;

➤ The volume of solidified lead droplets on the surface of the material influences the rate at which the solution manages to remove the lead. When the drops are too big, the contact surface of the lead with the cleaning solution is small and the cleaning speed decreases.

➤ Some chemical cleaning solutions like aqua regia, nitric acid and fluoboric acid were ineffective for lead removal or have damaged the protective oxide layer from the surface of the steel.

## R E F E R E N C E S

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