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ИЗСЛЕДВАНИЯ НА МИКРОСТРУКТУРАТА И СЪСТАВА НА ОБРАЗЦИ ОТ НЕРЪЖДАЕМА СТОМАНА В КОНТЕКСТА НА ЗНАЧИМОСТТА НА КРИТИЧНИТЕ СУРОВИНИ ЗА ДЪЛГОСРОЧНАТА И БЕЗОПАСНА ЕКСПЛОАТАЦИЯ НА ЯДРЕНИ ЕЛЕКТРИЧЕСКИ ЦЕНТРАЛИ

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MICROSTUCTURAL AND COMPOSITIONAL STUDIES OF STAINLESS STEEL SAMPLES IN THE CONTEXT OF CRITICAL RAW MATERIALS IMPORTANCE FOR LONG-TERM AND SAFE OPERATION OF NUCLEAR POWER PLANTS

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Критичните суровини са определени от Европейската комисия като материали с висока важност за икономиката на Европейския съюз и/или с висок риск за сигурността на доставките им от трети страни. Част от тези суровини се използват и в конструкционните материали, използвани в ядрените електрически централи. Характеризирането на материалите, съдържащи критични суровини и същевременно имащи отношение към ядрената безопасност и дългосрочната експлоатация, е важна дейност от обхвата на тези изследвания. В настоящата статия са представени данни от анализи на образци от неръждаема стомана от АЕЦ „Козлодуй“.

Long-term operation of nuclear facilities

The IAEA defines long-term operation of a nuclear power plant as operation beyond an established time frame set forth by license, term, design, standards, and regulations, which has been justified by safety assessment, with consideration given to life limiting processes and features of systems, structures and components [1]. The most important objective in nuclear power plants' operation is nuclear safety. Important considerations for defining the acceptable level of safety during long-term operation include the time period of long-term operation; the operational history and experience at the plant; the physical condition of the plant; the ageing of safety-related systems, structures and components; the degree of certainty about the long-term performance of safety components [2].

Currently long-term operation is considered worldwide since 64.8% of all power reactors are aged above 30 years. This share nominally represents 291 reactors with net installed electric capacity of 250.141 GW. The age distribution of the world power reactors fleet is shown on Figure 1. Long-term operation is a viable option to maintain nuclear power's role worldwide and particularly in the countries where it accounts for considerable share in the power generation (around or more than a fifth). Such countries are Belgium (37.5%), Bulgaria (31.3%), the Czech republic (35.8%), Finland (33.7%), France (76.3%), Hungary (52.7%), Republic of Korea (31.7%), Russia (18.6%), Slovakia (55.9%), Slovenia (38.0%), Spain, (20.3%), Sweden (34.3%), Switzerland (33.5%), Ukraine (56.5%), and the United States (19.5%) [3].

The long-term operation of nuclear power plants must ensure safe operation, manage the effects of ageing, and should provide at least the same extent of nuclear safety as that maintained during the design operational period [1].

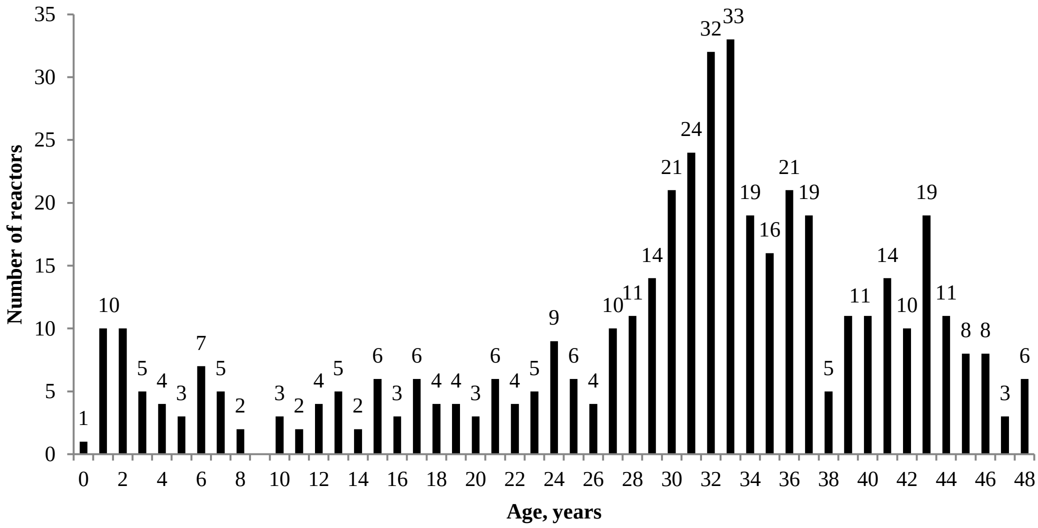


Figure 1. Age distribution of world power reactors [3]

Critical raw materials (CRM)

The European Commission has reviewed 54 non-energy materials which have been identified as important to EU’s economy. The materials under consideration include industrial minerals, ores, biotic materials, and processed or refined materials. The EU methodology used to estimate criticality has a combination of two assessment components: economic importance and supply risk. At the moment in which the research had been carried out twenty out of fifty four considered materials were classified as critical according to the EU criticality methodology: antimony, beryllium, borates, chromium, cobalt, coking coal, fluorspar, gallium, germanium, indium, magnesite, magnesium, natural graphite, niobium, platinum group metals, phosphate rock, rare earths, silicon metal, and tungsten [4]. The relationship between economic importance and supply risk for the 54 considered materials is illustrated on Figure 2.

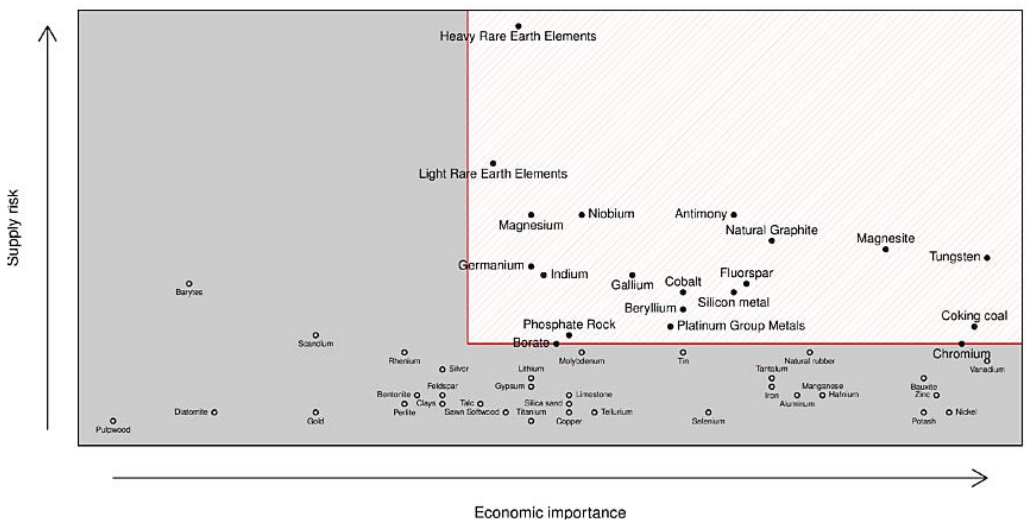


Figure 2. Critical raw materials for EU’s economy [4]

Critical raw materials in nuclear power applications

In the modern nuclear power plants (NPPs) with light water reactors more than 25 different main construction metal alloys are applied. Additional materials are present in concrete containments, instrumentation, tanks, pumps, support systems, control rods, moderators, neutron poisons, etc. Currently, nuclear power plants' general by-design operational period is 30-40 years, as the tendencies in nuclear power plant developments are focused on the life-time extension. Considerable number of existing reactors has operated for more than 30 years with the outlook for extending their operational life-times to up to 60 years (Figure 1). The new generation of nuclear reactors has to meet the following requirements [1]: longer operational lifetimes – up to, and in some cases, exceeding 60 years; technological efficiency and economic viability; strong focus on safety and reliability.

Meeting the abovementioned demands necessitates: (1) improving the construction materials and their components; and (2) corrosion control. In addition to meeting the requirements of long-term operation, materials in nuclear industry have to conform to other prerequisites, concerning their neutron absorption cross-section, service temperature, mechanical properties, neutron radiation resistance, thermal expansion, thermal conductivity, chemical compatibility, etc. High-nickel alloys, zirconium alloys, and stainless steels are used for various applications in nuclear power facilities. Stainless steels are used because of their good corrosion resistance. They are appropriate construction materials for components in contact with reactor coolant, such as circulating pumps, valves, pipes, heat-exchangers for chemical and volume control, condenser tubes, etc. The suitable properties of these key construction materials are obtained by adding critical raw materials (CRMs), such as Cr, Mo, Si, V, W, Mn, Mg, Nb, Co, Be, etc. Those materials must endure extreme operational conditions – neutron radiation, high temperatures and pressures, oxidizing and/or reduction media, tensions, electrolytic contact, etc. The CRMs used as alloying elements (e.g. Nb, Zr, Cr, W, V, Mo) are prone to supply risks that would have considerable impact on the economy of many European countries. The replacing construction materials would need to meet high requirements in terms of nuclear safety and long operational lifetime that could exceed 60 years [1,2,4,5].

Importance of chromium

Chromium has been included as a critical raw material in 2014 EU assessment due to greater concentration of supply in main producing countries, combined with the availability of more detailed statistics for the smaller producers. In 2017 (when the research was carried out) chromium was just over the supply risk threshold and was considered a borderline case (Figure 2). Since then the status of chromium has changed to not critical, as it was in 2014 [6].

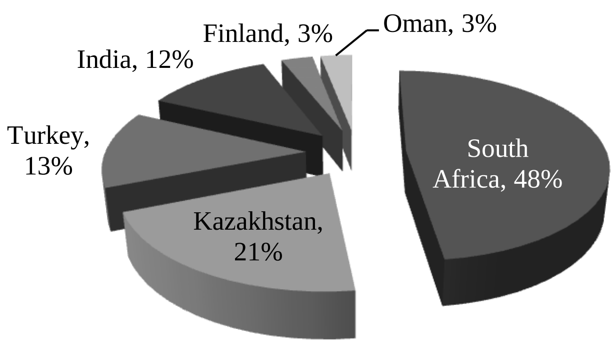


Figure 3. Global mine production of chromium, average 2010–2014 [6]

However, the importance of chromium remains: although it's the 22nd most abundant element in Earth's crust with an average concentration of 100 ppm, and an abundance of 92 ppm in the upper crust, its recycling rate is low and there are limited options for substitution, particularly in its main application, *i.e.* in stainless steels [4,6]. The main factor, determining chromium's criticality is the supply risk which can fluctuate around the threshold set by the European Commission's methodology. The majority of EU's chromium originates from third countries (88%), mainly from South Africa and Kazakhstan; just 3% of the world production takes place in the EU (Figure 3). The forecast average annual demand growth to 2020 for chromium is around 4.2% per year and it is evaluated that supply and demand in chromium market to 2020 would be balanced [4]. Its criticality score is shown on Figure 4. As it can be seen, the economic importance of the material is enormous. Moreover, according to the United States Geologic Survey, chromium has no substitute in stainless steels, its leading end use, or in super-alloys, its major strategic end use [7].

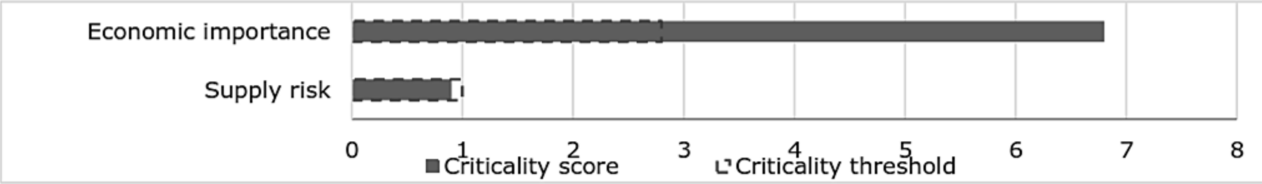


Figure 4. Economic importance and supply risk scores for chromium [6]

Research motivation

The results presented in the current paper have been obtained as a part of the project "Studies on the Importance of Critical Raw Materials for Long-term and Safe Operation of Nuclear Power Plants", carried out in February 2017 in the laboratories of Centro de Química Estrutural (CQE), Instituto Superior Técnico – Universidade de Lisboa, Lisbon, Portugal. The aim of the research was to gain understanding on the role of CRMs in nuclear industry which required clarification of the specifics of the system material-coolant-working parameters by investigating corrosion of construction materials exposed to working conditions in "Kozloduy" NPP. Samples of construction materials of importance for the reliable and safe long-term operation of NPPs with light-water reactors were investigated.

Steel 08X18H10T

Since "Kozloduy" NPP is designed and built using Russian technology, the eligible construction materials for nuclear power plants applications are outlined in the Russian standard for safe nuclear power equipment operation [8]. One of the main stainless steels used in Russian-designed nuclear power plants is 08X18H10T which is a Soviet/Russian austenitic chromium-nickel steel with wide range of applications in nuclear power plants. Its composition is regulated by the standard GOST 5632-72 and is as follows [9]: carbon – not more than 0.08 wt%; silicon – not more than 0.80 wt%; manganese – not more than 2.00 wt%; nickel – between 9.00 wt% and 11.00 wt%; sulphur – not more than 0.02 wt%; phosphorus – not more than 0.035 wt%; chromium – between 17.00 wt% and 19.00 wt%; copper – not more than 0.30 wt%; titanium – not less than 5 times carbon's concentration, not more than 0.70 wt%; iron – the remaining part. Its density is 7900 kg/m^3. The upper limits for alloying elements and admixtures in 08X18H10T's composition are shown on Figure 5.

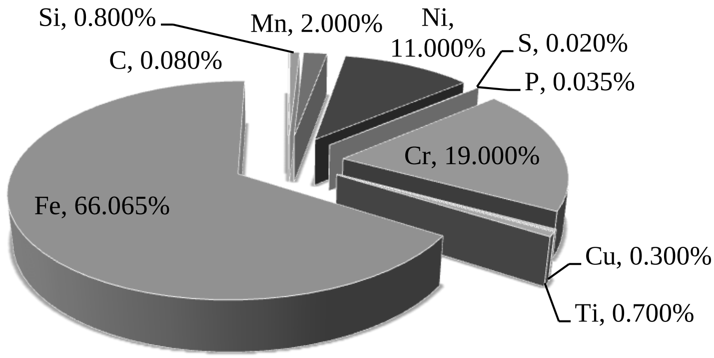


Figure 5. 08X18H10T chemical composition, wt% [9]

Results and discussion

The samples were taken from spent fuel storage pool's feed water system. The pipes were cut across, polished, and etched. The nominal working conditions of the material under normal operation of the power plant are listed in Table 1.

Table 1. Operational conditions of spent fuel cooling pool's feed water system

Working Medium		Chemically Purified Water
Material		Stainless Steel 08X18H10T
Working Parameters		
t_{min}	15.00	°C
t_{max}	45.00	°C
p_{min}	0.20	MPa
p_{max}	0.60	MPa
pH_{min}	5.50	
pH_{max}	8.00	
γ_{max}	1.00	µS/cm
C_{Cl-max}	0.05	mg/l

The performed microscopic studies on the samples reveal austenitic steel in annealed state. The austenitic structure is saturated with uniformly spread chromium, titanium, and nickel carbides. A uniform and homogenous distribution of elements without segregation can be observed. Microcrystals of carbides and oxides intercepted in different planes are spread into the structure. The composition of the steel corresponds to the standard specification. This is well illustrated by the material characterization (Figure 6 - Figure 7). The grain size of the material was found to be around 3-4 µm (Figure 8).

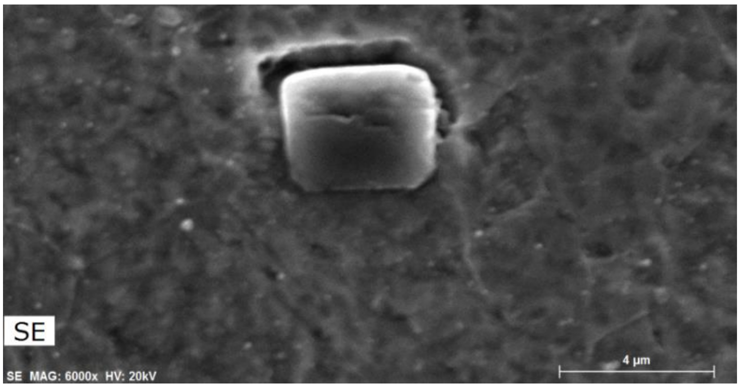


Figure 6. SEM Picture of the surface of the characterized material

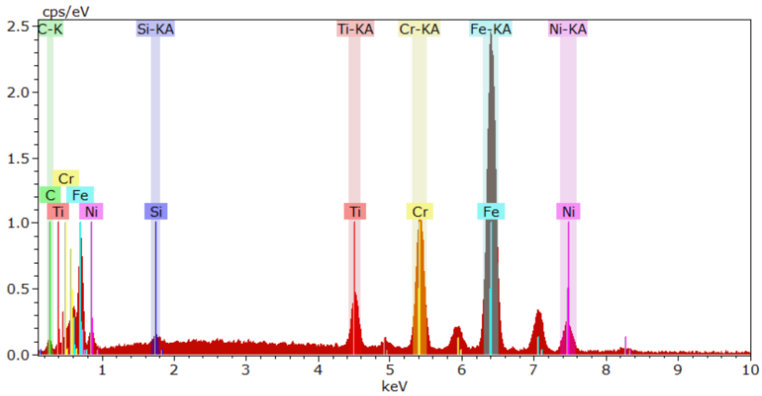


Figure 7. Material's spectrum

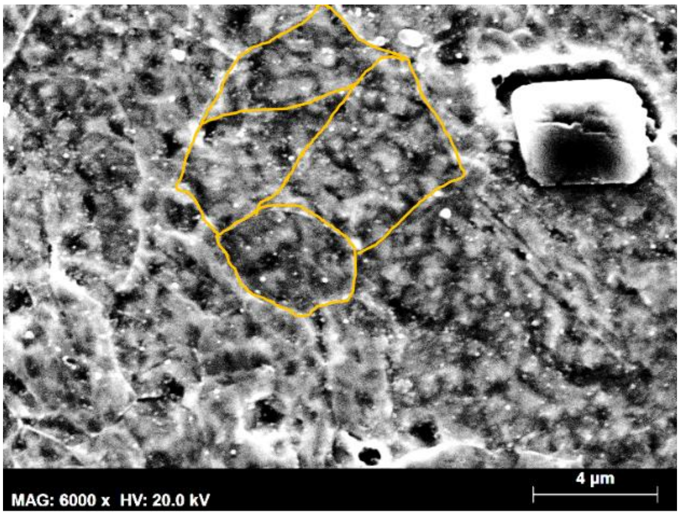
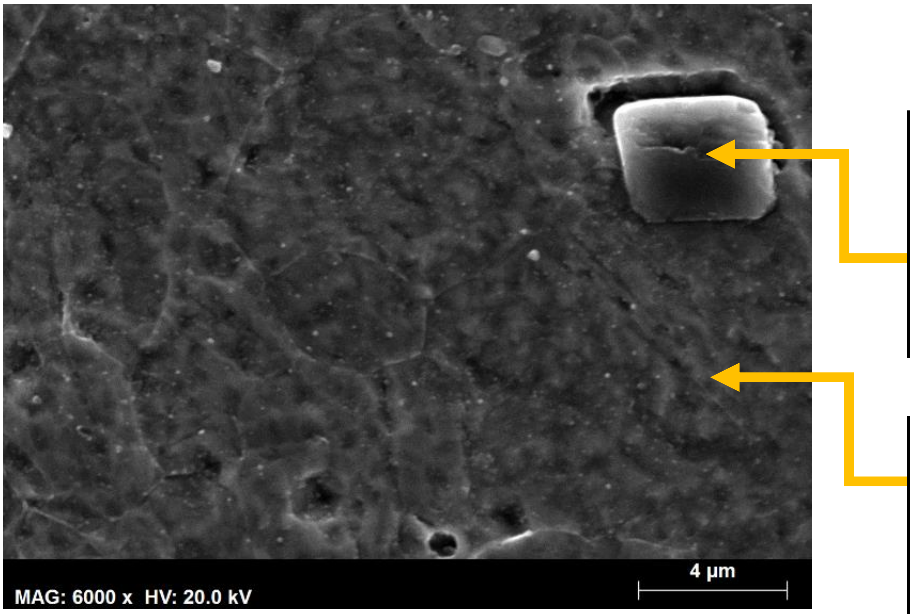


Figure 8. Grain size of the steel

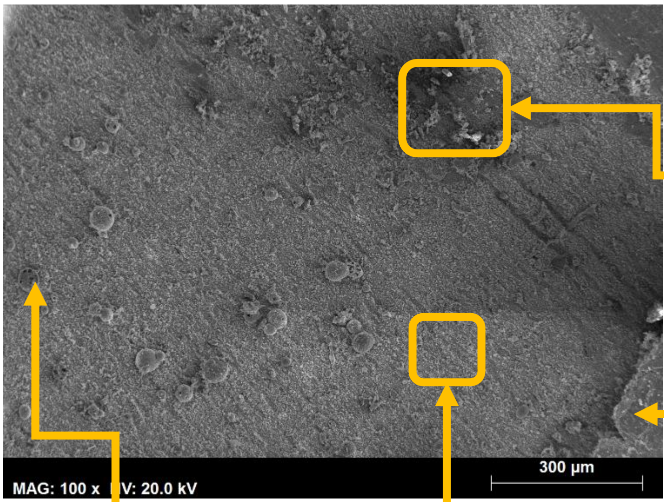
The examination of the steel's etched surface reveals the austenitic phase distribution as well as the distribution of the non-metal phases. Some separate pits due to single non-metal aggregates can be observed. Chromium depleted zones near grain boundaries most probably due to chromium carbide precipitations ($Cr_{23}C_6$) are revealed by an element compositional analysis. The formation of chromium carbides leads to corresponding compositional changes in the depth of grains. Initial inter-granular stress corrosion is observed on the borders of the complex carbides (Figure 9), which is the most typical corrosion process occurring at the austenitic steels caused by the susceptibility of their structure. Any corrosion damages due to some chemical or electrochemical interactions between the working medium and the constructional material were not observed. This is because the inner surface of the tubes is covered by a protective layer of chromium and iron oxides, combined with nickel and chromium ferrites, and chromium and iron complex carbides. Deposits of aluminosilicates, metal chlorides, as well as compounds of hardness are identified, most probably coming from water impurities. The composition of deposits was identified by spectroscopic studies. The results are shown on Figure 10. Because of the long-term operation of the studied material, single changes in initial stage were identified in the microstructure.



Carbon	15.2 %
Silicon	0.6 %
Titanium	5.7 %
Chromium	15.4 %
Iron	55.3 %
Nickel	7.8 %

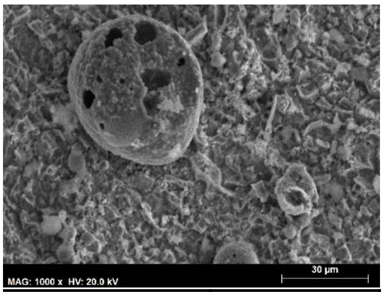
Carbon	52.5 %
Silicon	0.8 %
Chromium	8.7 %
Iron	33.3 %
Nickel	4.8 %

Figure 9. Chemical composition of characteristic points
on the material cross-section, at. %



Carbon	29.2 %
Oxygen	21.0 %
Sodium	3.5 %
Aluminium	4.0 %
Silicon	7.4 %
Chlorine	1.3 %
Potassium	0.5 %
Calcium	0.7 %
Chromium	6.7 %
Iron	23.4 %
Nickel	2.4 %

Carbon	31.0 %
Oxygen	8.5 %
Aluminium	1.5 %
Silicon	1.5 %
Chromium	10.3 %
Iron	41.2 %
Nickel	5.9 %



Oxygen	40.0 %
Chromium	5.5 %
Iron	18.2 %
Nickel	14.6 %
Carbon	21.8 %

Oxygen	11.4 %
Chromium	12.5 %
Iron	47.7 %
Nickel	4.1 %
Carbon	19.4 %
Silicon	1.1 %
Sodium	2.6 %
Manganese	1.1 %

Figure 10. Tube's inner surface and deposits of impurities characterization, at. %

Conclusion

The steel characterization results show that its composition matches the standard chemical composition. After long-term operation, single changes in the material's structure are identified, alongside initial signs of inter-granular stress corrosion. The material is found to be in annealed state with its inner surface covered with protective layer of complex iron and chromium oxides. Some sodium aluminosilicates and hardness components are observed on the inner surface, probably due to irregularities in water chemistry. Because of the protective chromium oxide layer the material has retained its working capacity during the entire period of operation.

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