

SOME RESULTS OF RESEARCH OF CHEMICAL PROCESSES IN A SUPERCRITICAL CONVECTIONAL WATER LOOP UNDER ELECTRON EXPOSURE

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The specific heat of water at the critical point increases abruptly and therefore supercritical water (SCW) can effectively cool a nuclear reactor, it would be promising to use SCW in nuclear energy. However, at high temperatures and due to radiolysis in which, along with hydrogen, oxygen, free electrons, hydrogen peroxide and free radicals are formed, SCW has increased corrosion activity.

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INTRODUCTION

Supercritical water consumption for cooling can be significantly less than subcritical water. Due to the high enthalpy of the coolant, equipment costs are reduced and, moreover, the efficiency of reactor increases by several percent, therefore, it is promising to use SCW in nuclear power [1]. However, at high temperatures and due to radiolysis, SCW has an increased corrosive activity. At the critical point, the dielectric constant of the SCW is close to zero (organic substances dissolve perfectly and inorganic ones precipitate), which puts it on a par with organic solvents. SCW is an effective medium for carrying out chemical reactions. Radiation exposure in which, along with hydrogen, oxygen, free electrons, hydrogen peroxide is formed and free radicals contribute to chemical transformations of substances. To use SCW in nuclear power, it is necessary to carry out corrosion studies and study the chemical transformations of substances in the SCW environment under the influence of radiation.

1. SCOPE OF USE OF SUPERCRITICAL WATER

There are numerous publications on the practical application of supercritical water excluding applications in power engineering. Perhaps the largest number of publications is devoted to the destruction of organic substances in the SCW environment. Moreover, the destruction takes place both with the injection of oxidants (oxygen, hydrogen peroxide) and without them. Thus, it has been established that SCW itself is a reagent. Simultaneously with oxygen in SCW there is a certain concentration of hydrogen, which significantly affects the properties of SCW in the environment of which the processes of decomposition and formation of water molecules occur simultaneously [2].

The destruction of organic matter in wastewater in SCW produces hydrogen and, at the same time, a certain amount of char [3]. Treatment of petroleum products in SCW leads to their desulfurization with simultaneous release of hydrogen sulfide [4]. Oil recovery at best reaches 50%; it is promising to use SCW fluid to liquefy and displace oil with its simultaneous refining [5]. Particularly toxic substances, for example, rocket

fuel heptyl (asymmetric dimethylhydrazine), degrades in SCW mainly with the formation of nitrogen, but at least 400 substances have been identified along the way [6]. Since inorganic salts are insoluble in SCW, it is used for water desalination [7]. The influence of SCW explains volcanic processes (explosions, landslides due to lubrication in the form of SCW) and such a terrible phenomenon as a "scorching cloud" when a cloud of sand (ash) and superheated steam with a temperature of 500° rushes along the earth's surface at a speed of 500 km/h burning everything in its path [8].

2. STUDY OF THE PROPERTIES OF SUPERCRITICAL WATER IN A CONVECTION LOOP

The study of the properties of SCW undertaken by us consisted in the use of a convection loop made of a thick-walled stainless tube. An irradiation chamber was welded into the loop for SCW processing with an electron beam. Water samples were taken from time to time and some SCW parameters were determined. A number of metals were identified in the water. The sodium content was 0.5...0.6 mg/l, the same in distilled water. Unfortunately, sodium is difficult to get rid of in water and chemicals. The potassium content is about half that of sodium. The content of chromium was 20...26 µg/l, copper 39...62 µg/l, iron 200...500 µg/l, manganese 12...15 µg/l, nickel 15...23 µg/l. Determinations were carried out by emission and mass spectrometric methods. The content of heavy metals in distilled water is noticeable, but an order of magnitude lower than in water from the loop (determined by corrosion), and for chromium it is two orders of magnitude lower. As an example, Fig. 1 shows the chromium content in SCW.

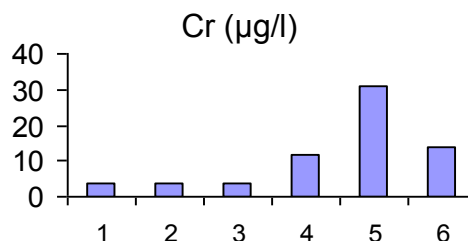


Fig. 1. Graphs of changes in chromium content in water from the loop in the period 17-22.08.2019

During the experiments with the loop, trace amounts of ethyl alcohol were introduced into the circulating water. After that, the circulating water acquired an odor and it was found that there is an abrupt increase in the electrical conductivity of water, while the pH drops from 5.8 to 3.5 and the oxygen content decreases to almost zero. Gas chromatographic analysis of water was carried out, in which, in addition to ethanol, ketones (acetone, methylethylketone, methylisopropylketone) and ethyleneglycolpropylether (propylcellosolve) were found. Radioactive radiation favors the transformation of substances. It can be assumed that oxygen in SCW is formed during the destruction of water and was spent on the oxidation of such a good reducing agent as ethanol. During ethanol oxidation, substances with acidic properties (unfortunately not identified) were probably formed, which led to a decrease in pH and an increase in conductivity. SCW also acidifies chromium due to its oxide (VI), which passes into water during corrosion.

Typical changes in the SCW electrical conductivity, pH, and dissolved oxygen content are shown in Figs. 2-4.

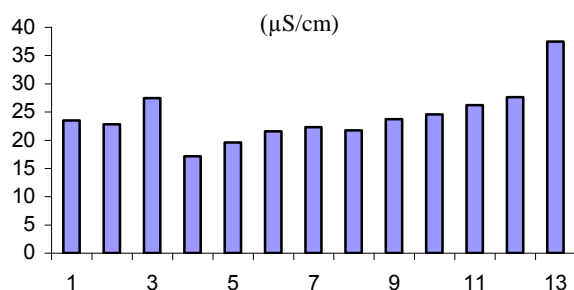


Fig. 2. Graph of average changes for a 12-hour change in the conductivity values ($\mu\text{S}/\text{cm}$) of water from the loop in the period 17-23.08.2019

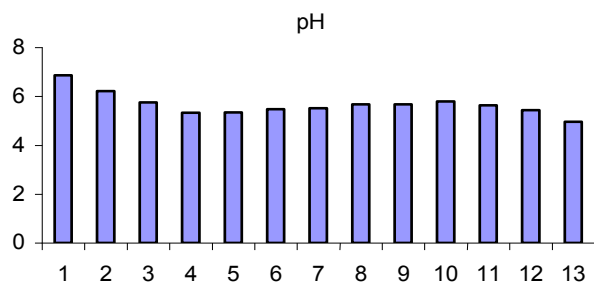


Fig. 3. Graph of average changes for a 12-hour change in the pH values of water from the loop in the period 17-23.08.2019

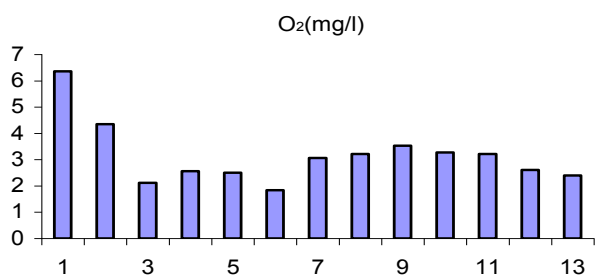


Fig. 4. Graph of average changes for a 12-hour change in oxygen values in water from the loop in the period 17-23.08.2019

CONCLUSIONS

There are prospects for the use of SCW in nuclear power, however, the issues of corrosion in SCW at high temperatures and in the presence of radiolysis products remain unresolved. When the convection loop with the irradiation chamber operates, metal ions and, first of all, chromium ions pass into the SCW, which lowers the pH of the circulating water. When organic substances are added to water, SCW is significantly acidified and oxygen is almost completely removed.

Considering that SCW is used as a reaction environment and as a reagent for neutralizing organic waste, upgrading chemical products, it is useful to conduct research on the conversion of substances into SCW, taking into account the effect of radiolysis products, as well as to displace oil from formations.

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ДЕЯКІ РЕЗУЛЬТАТИ ДОСЛІДЖЕНЬ ХІМІЧНИХ ПРОЦЕСІВ У НАДКРИТИЧНІЙ КОНВЕКЦІЙНІЙ ВОДНІЙ ПЕТЛІ ПРИ ОПРОМІНЕННІ ЕЛЕКТРОНАМИ

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Питома теплоємність води в критичній точці стрибкоподібно збільшується, і тому надкритична вода (НКВ) може ефективно охолоджувати ядерний реактор. Було б перспективно використовувати НКВ у ядерній енергетиці. Однак при високій температурі і за рахунок радіолізу, при якому поряд з воднем, киснем, вільними електронами утворюються пероксид водню і вільні радикали, НКВ має підвищену корозійну активність.

НЕКОТОРЫЕ РЕЗУЛЬТАТЫ ИССЛЕДОВАНИЯ ХИМИЧЕСКИХ ПРОЦЕССОВ В СВЕРХКРИТИЧЕСКОЙ КОНВЕКЦИОННОЙ ВОДНОЙ ПЕТЛЕ ПРИ ОБЛУЧЕНИИ ЭЛЕКТРОНАМИ

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Удельная теплоемкость воды в критической точке скачкообразно увеличивается, и поэтому сверхкритическая вода (СКВ) может эффективно охлаждать ядерный реактор. Было бы перспективно использовать СКВ в ядерной энергетике. Однако при высокой температуре и за счет радиоллиза, при котором наряду с водородом, кислородом, свободными электронами образуются пероксид водорода и свободные радикалы, СКВ имеет повышенную коррозионную активность.