CORROSION OF REACTOR MATERIALS

The two most "modern" fields of technology, nuclear and space engineering, are placing drastically increased demands on numerous materials; they have to conform to extremely rigorous specifications, in which new physical and chemical properties have been added to the old ones. One of the necessary characteristics is increased corrosion resistance. In fact, corrosion resistance has often been described as the foremost problem in the choice of reactor materials.

Reactor materials include nuclear fuels (mainly uranium, but also plutonium and thorium), the cladding in which the fuel is contained and pipes and vessels in which coolants circulate (a large variety of steel, aluminium, zirconium and other alloys), moderators (graphite, beryllium, etc.), shielding (concrete of varying composition), and metals used for mechanical reactor components. All these are subject to particularly heavy corrosion owing to the fact that they are exposed to coolants at high temperatures and pressures and to irradiation, and the fact that radiation increases the susceptibility of certain materials to corrosion.

Heavy corrosion may impair the functioning of reactor parts and reduce their lifetime. This, in turn, would increase the shut-down periods of reactors for maintenance and repair work, with a corresponding rise in operating cost. This factor is of considerable importance in view of the large capital outlay on reactors.

A second consideration in this connection is the possibility of hazards, which may arise from the pollution of the primary cooling system with highly radioactive fission products resulting from severe damage to fuel element claddings. On the other hand, a corrosion-induced leak in the primary circuit may lead to heavy contamination of the adjacent installations or even of the surroundings. Products of such corrosion may not only impair the flow of cooling liquids within the heat exchanger and cooling systems of reactors; they may also become radioactive themselves and contaminate the whole system. This could give rise to considerable radiation hazards. In addition, radioactive contamination may necessitate a prolonged decontamination shut-down of a reactor, with corresponding financial loss.

Since, broadly speaking, the efficiency of a reactor increases with precisely those factors which also increase corrosion (primarily rise of temperature), corrosion resistance assumes considerable economic importance.

Much operational experience and many experimental results have accumulated in recent years regarding corrosion of reactor materials, particularly since the 1958 Geneva Conference on the Peaceful Uses of Atomic Energy, where these problems were also discussed. It was, therefore, felt that a survey and critical appraisal of the results obtained during this period had become necessary and, in response to this need, IAEA organized a Conference on the Corrosion of Reactor Materials at Salzburg, Austria (4-9 June 1962). It covered many of the theoretical, experimental and engineering problems relating to the corrosion phenomena which occur in nuclear reactors as well as in the adjacent circuits. Some 200 experts from 23 countries took part in this meeting.

Behaviour of Steel

Several of the papers presented at the conference dealt with the behaviour of steel. H. Inouye (USA) reported on studies on high temperature reactions of certain types of stainless steel in helium with low concentrations of carbon dioxide and carbon monoxide. This research was part of the fuel development programme for the Experimental Gas-Cooled Reactor.

R. Darras, D. Lecleroq and H. Loriers (France) described corrosion effects of carbon dioxide on structural steel at average temperatures of between 450°C and 550°C under pressure. The varying compositions of both the steel and the gases used gave revealing but often very widely varying results.

H. E. McCoy Jr. (USA) discussed various types of gas-metal interactions and their effect upon the service performance of metal. These investigations were undertaken to render possible an increase in the operating temperature of gas-cooled reactors by selecting suitable structural materials and fuel element claddings. The experiments were carried out over a temperature range of 700°-900°C with stainless steels, nickel-based alloys and refractory metals in environments of argon, hydrogen, carbon monoxide, carbon dioxide, nitrogen, air and oxygen. Studies on the kinetics of electrode processes of low-alloy chrome and chrome-nickel stainless steels and aluminium alloys at temperatures of up to 300°C and pressures of up to 87 atmospheres were described by V. V. Gerasimov (USSR). The data obtained from these studies made it possible to forecast the corrosion behaviour of structural materials at critical temperatures in water of any composition.

V. S. Lyashenko, V.V. Zotov and V.A. Ivanov (USSR) reported on experimental work on the resistance to corrosion of various construction steel samples in a stream of liquid sodium at temperatures of 600°C and 700°C. Various impurities had a significant influence on corrosion resistance of these materials, either increasing or lowering it.

F. M. Lang and P. Magnier (France) gave an account of experiments on the corrosion of graphite by coolant gases. It was found that the corrosion effect on numerous highly purified carbons and graphites of widely different origins was practically the same. Humidity and the presence of hydrogen showed a very definite influence; the speed of oxidation depended on the temperature.

The use of carbon-14 for the study of carbon transport in the radiation-induced reaction between carbon and carbon dioxide in a graphite-moderated, carbon dioxide-cooled reactor was described by T. B. Copestake and F. S. Feates (UK). Carbon-14 was incorporated into graphite and the gasification of the graphite was studied by measuring the carbon-14 activity.

Aluminium and Zirconium Alloys

Corrosion of aluminium alloys in high temperature water (260°-315°C) depends partly on the conditions under which the tests are run. According to J. E. Draley and W. E. Ruther (USA), corrosion rates largely vary when there is a high rate of flow of water past metal surface. They pointed out that seemingly minor variations in conditions cause large changes in corrosion rate. Also, the silicon content of aluminium-nickel-iron alloys was found to have an important influence on their corrosion behaviour. Alloys with extremely low silicon content behaved better than those with a more typical silicon content.

On the other hand, K. Videm (Norway) discussed alloys containing about ten per cent silicon in addition to the one per cent nickel normally incorporated in aluminium for high temperature performance. These alloys were found to be more corrosion-resistant than the ordinary ones.

M. J. Brabers (Belgium) described investigations, made by means of a so-called "transitometer", into the formation of oxide layers on high purity aluminium and its alloys. The "transitometer" comprises a constant current source and a switch which opens the circuit at certain pre-set voltages of the electric current and of an electronic timer working simultaneously.

Zirconium, one of the most important nuclear materials used in producing corrosion-resistant alloys, was discussed by a number of experts.

A group of Soviet scientists, I. L. Rosenfeld, Yu. P. Olkhovnikov and A. A. Sudarikova, reported on the effects of the composition of water on corrosion of zirconium alloys at high temperatures and pressures. Alloys of zirconium with niobium and also with lead, iron, nickel and niobium have a high corrosion resistance in pure distilled water at 360° C. The presence of insignificant concentrations of certain ions in the water, which under normal conditions would be absolutely harmless, induces intensified corrosion of zirconium alloys at high temperatures. On the other hand, certain other ions, which activate reactions under normal conditions, have practically no effect on the corrosion of zirconium alloys at the temperatures in question. The varying nature of the effect of the ions was stated to be connected with their influence on the characteristics of the protective films formed on the surface of zirconium alloys.

Studies on corrosion resistance of a zirconium-niobium alloy were also dealt with by S. B. Dalgaard (Canada). He said that because of the improved mechanical qualities which this alloy showed after appropriate heat treatment, it was intended to use it for the fabrication of pressure tubes in Canadian power reactors, in place of the Zircaloy used at present.

The corrosion of Zircaloy in various alkaline media at high temperature - which is of interest in pressurized-water reactors - was the object of a study by H. Coriou, L. Grall, J. Neunier, M. Pelras and H. Willermoz (France). The purpose of using these media is to make the corrosion products more filterable and so to reduce considerably the contamination of the circuits. The authors showed that a "critical threshold" exists in regard to lithium hydroxide concentrations, above which very rapid corrosion takes place, and that this threshold is greatly influenced by temperatures. For ammonia no such threshold was noted.

The effect of reactor irradiation on the oxidation of zirconium alloys in steam was the subject of a paper presented by B. Cox and R. C. Asher (UK). According to their findings, considerable variations exist in the formation of oxide films, dependent on the temperature and on the nature of the neutron flux. It was observed that the growth of thin oxide films could be attributed to irradiation with gamma rays.

J. Debuigne and P. Lehr (France) discussed the kinetics of oxidation of non-alloyed zirconium in a dry oxygen atmosphere at temperatures of between 600°C and 850°C. They showed that the formation and growth of a surface oxide film is accompanied by considerable diffusion of the oxygen in the underlying metal - a phenomenon which makes the metal more brittle.

The effect of hydrogen on metals which are normally covered and more or less protected by an oxide layer was discussed by J. S. L. Leach and A. Y. Nehru (UK).

Problems in Advanced Reactors

Since the prospect of economic nuclear power depends to a considerable extent on the possibility of developing breeder reactors, particular importance attaches to corrosion effects caused by molten plutonium fuel. B. J. Thamer, R. P. Hammond, R. M. Bidwell, C. C. Burwell and J. E. Kemme (USA) pointed out that molten plutonium alloys may combine some of the advantages of fluid fuels with the high breeding ratios that are possible with fast plutonium reactors. The precondition for their utilization is the development of the appropriate container material.

The theoretical aspect of corrosion by liquid metals was discussed by J. R. Weeks and C. J. Klamut (USA).

A reactor with the fuel material homogeneously distributed in molten fluoride salts is considered to be a promising concept for future power reactors. For the Molten Salt Reactor Experiment at the Oak Ridge National Laboratory, USA, a high-strength nickel-base alloy has been developed. J. H. De Van and R. B. Evans (USA) described the results of several tests to demonstrate the excellent corrosion resistance of this material to molten fluorides at high temperatures.

Lithium has been regarded as a promising coolant for power reactors for some time. J. R. Di Stefano and E. E. Hoffman (USA) reported on experiments on the compatibility of various container materials with molten lithium.

Special interest attaches to the use of organic-cooled and -moderated reactors because of certain superior physical and chemical properties which organic liquids possess, as compared to water. One of these properties is the low corrosion rate shown by organic coolants when used with common materials and with metallic nuclear fuels.

Corrosion effects with organic coolants were described by W. E. Parkins (USA), who gave the results of tests carried out on different types of steel, aluminium, zirconium, magnesium and some of their alloys. The results showed that all the materials tested are essentially inert to the organic coolants in their pure form; corrosion occurs only as a result of certain impurities. Magnesium corroded severely in the presence of small amounts of water; hydrogen attacked zirconium. No increase in the corrosion rate due to the presence of radiation was noted, but it was pointed out that radiation produces free hydrogen as well as certain organics which are then capable of reacting with oxygen to form corrosive compounds.

Other Procedures and Summing Up

P. J. Gellings (Netherlands) suggested a procedure which would make it possible to follow the corrosion of test pieces inside a reactor or even of the reactor material itself without the need of their being removed for inspection. Decontamination of reactors or of parts of the primary system was dealt with in a paper by J. A. Ayres (USA). Decontamination itself is essentially a controlled corrosion process in which the film is removed along with a small amount of the underlying metal. Excessive corrosion is suppressed by the addition of suitable inhibitors. Corrosion is caused not only directly by the decontamination process, but also by an enhanced rate of attack during subsequent operation as a result of the removal of the protective film.

M. J. Brabers, chairman of the last session, in a summing-up of the discussions, said:

"In general, results from different countries agreed rather satisfactorily or complemented one another very well. Great progress has been made in the improvement of corrosion resistance to reactor materials; some years ago, for example, 150°C was considered the maximum temperature for aluminium alloys. This week the figure 350°C was quoted, representing an increase of 200 degrees which is quite considerable. Zirconium alloys also show some improvements. We have heard about the beneficial effects of niobium and copper. It is doubtful whether, in this case, increasing the niobium content will further improve the corrosion resistance in view of the enormous effects of the heat treatments. If the improvements in corrosion resistance continue at the rate achieved over recent years, it may well be less the corrosion than mechanical aspects which will be the determining factor in atomic energy within several years. This point may already have been reached in the case of aluminium, but I am sure that later on still much higher temperatures will be given. Irradiation may have many effects like face changes, dislocations, etc. In that respect the material presented was still limited, but as somebody remarked, corrosion without any irradiation is already difficult enough to understand. With irradiation as well, a whole series of complications is added to the problems."

Čestmír Šimáně, Director of IAEA's Division of Technical Supplies, speaking at the closing session, said that the papers dealing with technological aspects had been more impressive than the theoretical contributions. The conference, he said, had shown how little we actually knew regarding corrosion, but this very realization was a factor of progress.