NEA/CSNI/R(92)5
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Workshop on

IODINE CHEMISTRY IN REACTOR SAFETY

Tokai-mura (Japan)
11-13 September 1991

Organised by

OECD NUCLEAR ENERGY AGENCY

in collaboration with

JAPAN ATOMIC ENERGY RESEARCH INSTITUTE

SUMMARY AND CONCLUSIONS

COMMITTEE ON THE SAFETY OF NUCLEAR INSTALLATIONS
OECD NUCLEAR ENERGY AGENCY
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FOREWORD

The Third OECD (NEA) CSNI Workshop on the Chemistry of Iodine in Reactor Safety was organised from 11th to 13th September 1991, in Tokai-mura, in collaboration with the Japan Atomic Energy Research Institute (JAERI).

The importance of the behaviour of iodine, in terms of radiological effects on the environment, is well recognized. It is for this reason that safety analysis of a water-cooled reactor takes into consideration the generation and release of iodine from nuclear fuel to the environment. Every effort should be made to minimise the release based on the concept of as low-as-reasonably-achievable (ALARA). A large number of experiments as well as analyses have been done in the past years to understand iodine behaviour under a range of operational and accident conditions. Nuclear reactor regulations in the OECD Member countries reflect findings and results from programmes conducted worldwide.

The low radioiodine release observed in the TMI-2 accident has drawn much attention to the rate of generation, chemical forms and reactions of fission products in reactor accidents. These would determine the amounts of fission products released to the environment, generally called the "source term", during a severe accident which results in severely damaged fuel. The findings from the TMI-2 accident lead to the re-evaluation of source terms in a severe accident, especially that of iodine. A number of reports have been published on such re-evaluations of accident source terms.

The NEA Committee on the Safety of Nuclear Installations reviewed the international activities in this area; a summary report was issued in 1986. It became apparent from these studies that the data base on fission product chemistry was not sufficient for the requirements of safety analyses for water-cooled reactors.

This conclusion motivated the Committee on the Safety of Nuclear Installations to hold the First CSNI Workshop on Iodine Chemistry in Reactor Safety at the Harwell Laboratory, UK, in 1985, which was followed by the Second Workshop in Toronto, Canada, in 1988. The two Workshops provided a forum for exchanging research results and views on iodine chemistry among experts of Member countries and a unique opportunity for safety analysts to discuss their requirements with chemists. At each Workshop, the Programme Committee issued conclusions and recommendations for future work. One of the recommendations of the Second Iodine Workshop was to hold the Third Workshop within two to three years to review progress and developments.

In view of the importance of fission product behaviour, especially in severe accidents, and as a result of recommendations from the Second Workshop, the Japan Atomic Energy Research Institute offered to host the Third Workshop at its Tokai Research Establishment.

At the Workshop, an effort was made to integrate all information for better use by safety analysts. There is no doubt that a lot of information on iodine behaviour has been accumulated, but in many cases this information needs to be co-ordinated and well organised for safety analyses of nuclear reactors. It is essential that the results of laboratory studies and integral experiments together with modelling activities are well co-ordinated. Therefore, the goal was:

- to review the knowledge and understanding of the chemistry of iodine of relevance to the prediction of its behaviour in nuclear reactors during a range of operational and accident conditions;

- to define those areas of chemistry which are important but poorly understood and require further study.

As shown by the conclusions of the Workshop, there is no doubt that this objective was widely attained.

JAERI gave very generous hospitality to the Workshop; special thanks are due to Dr. K. Soda, Dr. M. Saeki and Dr. J. Sugimoto who have invested a lot of work and effort in the preparation of the meeting. We also would like to express our gratitude to the members of the Programme Committee, Professor K. Ishigure (Chairman of the Workshop), Dr. K.-H. Neeb (represented by Dr. W Morell), Dr. R.L. Ritzman, Dr. M. Saeki, Dr. H. Sims, Dr. K. Soda, Mr. L. Soffer, Dr. J. Sugimoto, Dr. A.C. Vikis. Their efforts and advice have strongly contributed to the success of the Workshop.

J. Royen
NEA Secretariat

SUMMARY AND CONCLUSIONS

The Third CSNI Workshop on Iodine Chemistry in Reactor Safety was held at Tokai-mura, Japan on September 11 to 13, 1991. It was hosted by the Japan Atomic Energy Research Institute (JAERI). About sixty experts attended the Workshop, from ten countries and two international organisations; these included for the first time two experts from the U.S.S.R. Twenty-nine papers were presented in five sessions on various aspects of iodine chemistry in reactor safety. The proceedings will be published by JAERI under separate cover.

Examination of the programmes of the three Iodine Workshops held so far, shows that the trends in research and development in this field have shifted significantly since 1985:

(1) from homogeneous to heterogeneous systems,
(2) from inorganic to organic iodide species,
(3) from fundamental to integral tests, and
(4) from scientific to engineering approaches.

These observations have important consequences for further developments in this area, as reflected in the following conclusions and recommendations:

(1) Substantial progress has been made in understanding and predicting the behaviour of iodine in the containment building of a reactor following an accident, such as a loss-of-coolant accident. Collaboration between scientists and engineers in designing and analyzing integral and fundamental tests is necessary for further progress in this field.

(2) In spite of recent progress, fission product chemistry is still one of the main contributors to source term uncertainties; further research is needed in this field, in particular in the areas of organic compound interactions and surface effects.

(3) Dialogue between safety analysts and chemists is essential to identify the importance to risk of chemical phenomena and to prioritize safety issues involving fission product chemistry.

(4) Much of the homogeneous solution chemistry is understood; particularly important exceptions are rates and mechanisms for iodine hydrolysis, hydrogen peroxide reactions and the role of organics.

(5) Interactions between iodine vapour and bulk material aerosols can occur and have significant effects on iodine speciation and transport.

(6) Iodine volatility within containment increases with decreasing pH, but, in the presence of radiation, it is not sensitive to the initial aqueous iodine species.

(7) There is further need for the development/validation of existing models and codes against realistic integral tests. However, separate effects experiments must also be performed to both guide and help rationalize the data for the large integral tests.

(8) A variety of surface interactions involving iodine can and probably will affect its transport and volatility in accident situations. Dealing with surface reactions was identified as one of the most significant uncertainties in models and codes.

(9) Suspended CsI aerosols can be oxidized to iodine during hydrogen burns under dry conditions. However, modest steam concentration (10 %) suppresses CsI oxidation to I_2. Additional research on this issue is recommended.

(10) Intervention remains an important issue. It has been shown that high pH is favourable, but the minimum pH required to suppress volatility is uncertain.

(11) An evaluated kinetic database is being issued and should be maintained. Some efforts should be devoted in the future to assess the temperature dependence of the reactions included in this database. Also, a sensitivity analysis should be conducted to reduce the number of chemical reactions to the most important ones.

(12) Studies should be broadened to examine fission products other than iodine that are important to risk such as cesium and tellurium. It is recommended that the next Workshop, if held, should also focus on these fission products. The need for and the scope of another Workshop should be reviewed in two years time.

The following is a summary of papers presented at the meeting, including several points of direct relevance to reactor safety:

Probabilistic safety assessment (PSA) is an important and effective tool to identify areas of uncertainties associated with source term evaluations of a nuclear reactor accident and to prioritize research areas. It was pointed out at the Workshop that fission product chemistry, particularly modelling of organic compound interactions and surface interactions, is one of the sources of uncertainties; further research is needed in this area. Codes need improvement in modelling fission product behaviour as well. However, the relative importance of each phenomenon to nuclear safety should be carefully examined before detailed investigations are initiated. Therefore, a dialogue between safety analysts and researchers in chemistry is essential in order to identify and prioritize safety issues regarding fission product chemistry.

National and international programmes carried out in the past have been extremely valuable; future programmes will also be of importance, not only in the OECD area, but also in the rest of the world. At the Workshop, a lot of work done in Canada, Japan and the United Kingdom was presented. The ACE programme focused on several key uncertainties such as radiolysis effects, hydrogen combustion effects, interactions with aerosols and interactions with surface coatings. The Commission of the European Communities (CEC) also conducts extensive research on fission product chemistry primarily under the

PHEBUS-FP programme. Regulatory application of the current technology may lead to a revision of source term criteria in the U.S.A. It was agreed at the Workshop that worldwide communication among safety experts is clearly useful to further reduce the risk of a nuclear reactor accident.

Papers on homogeneous chemistry covered effects of silver on radiolytic methyl iodide formation and destruction and also effects of pH, organic materials and their concentration on radiolysis of iodine solution. An analytical description of the mass transfer and kinetics aspects of the JAERI VITA facility was presented. This was followed by a related paper on effects of radiolysis in boiling solutions, where mass transfer is also important. Another paper gave valuable measurements of rate constants for reactions of the OH radical with I^-, the reaction of H_2O_2 with the hydrolysis products of I_2 and the rate of reaction of I_2 with OH^-.

The conclusions were that much of the homogeneous solution chemistry of iodine was understood. Particularly important exceptions are rates and mechanisms of iodine hydrolysis, and of reactions of H_2O_2 with molecular iodine and its hydrolysis products. The key area of uncertainty is now the role of organic solutes on the pH behaviour, organic iodine production and inorganic iodine behaviour in a radiation field. The combination of mass transfer with reaction was shown to be important to the rate of evolution of iodine as well as the partition coefficient.

Papers on chemistry at surfaces including vapour-aerosol interactions showed that surfaces can have an important impact on iodine behaviour in severe accident environments. A useful experimental technique for determining the kinetics of vapour-aerosol reactions was described and data for the reaction of iodine with cadmium and silver were given. An approach for interpreting data on organic iodide formation at surfaces was also presented. Three papers showed the value of performing separate effects laboratory experiments to help plan and rationalize integral tests. These papers also confirmed the advantage of maintaining alkaline pH conditions in water reservoirs to limit iodine volatility and associated surface interaction effects. New measurements of the rate of I_2 deposition on epoxy paint were presented and rationalized using semi-empirical expressions. It was concluded that a considerable amount of new data are available showing trends in surface processes and effects which can now be used to improve and validate iodine models and codes.

Five papers regarding integral experiments conducted in Canada, the FRG, the U.K. and the U.S. were presented. Results from the ACE programme showed the importance of maintaining high pH in controlling low iodine volatility in containment. Once the solution becomes acid, iodine volatility is only slightly decreased if the solution is changed to alkaline. This has important implications for a strategy of pH control within containment and implies that the pH must be kept alkaline from the beginning. Measured iodine aerosol deposition rates in a large steel vessel were rapid, with about 98 % of the mass removed with a removal half-time of 40 minutes. Conversion of CsI aerosol to I_2 was measured under hydrogen combustion conditions. With no steam present, about 15 % of the CsI was converted to I_2, whereas, when 10 % steam was present, less than 0.5 % of the CsI was converted. Evidence was seen of chemical reactions of CsI and CsOH with boric acid to form $CsBO_2$ and HI. In addition, iodine release was measured for iodine dissolved in water in high pressure tubes. Under pipe rupture conditions, less than 1 % of the iodine was released from a compartment. This finding has application for steam generator tube rupture accidents.

Most prominent amongst the conclusions/recommendations of the Second CSNI Workshop on Iodine Chemistry was the wish to test models and codes against large-scale, realistic, integrated tests. Thanks to a number of national and international activities during the last three years, the above wish has been largely fulfilled as evidenced by the number of papers presented on this topic. Such tests provided the basis for further development of the IMPAIR-2 code, which now includes an iodine/aerosol interaction submodel and improved submodels for dealing with the iodide reactions, high molecular weight organic iodides, and deposition/revolatilization. Data from the University of Tokyo, Oak Ridge National Laboratory, AECL Research, and AEA Technology were used to test the INSPECT code. The LIRIC model was further developed and tested using data from the Radioiodine Test Facility (RTF) and a preliminary organic radiolysis submodel was developed through a U.K./Canada collaboration. Finally, the ACE-RTF programme provided an opportunity for a code comparison exercise for the INSPECT, LIRIC, IMPAIR, IODE and TRENDS codes. In addition to the predictive capabilities of codes, their usefulness in identifying areas of uncertainty in iodine chemistry was demonstrated during this session.

A first attempt was made to apply the iodine code IMPAIR-2 to a source term analysis for a LWR plant. For this purpose the IMPAIR-2 code was inserted into a code package system. The thermo-hydraulic boundary conditions calculated with the codes in the package give input data to the IMPAIR-2 computation of the iodine behaviour for every compartment. An encouraging first approach was made to model the efficiency of containment spray systems by considering the effects of chemical reactions on mass transfer rates. As a next step the spray removal method should be included into the containment iodine codes. In order to arrive at a European standardized basis for modelling the iodine behaviour in calculations of radiological consequences of design basis accidents, the CEC has initiated studies to integrate the different boundary conditions in the existing PWRs and their influence on iodine behaviour (from the release from the fuel to the release to the environment). Uncertainties regarding the volatility of aqueous HOI were discussed.