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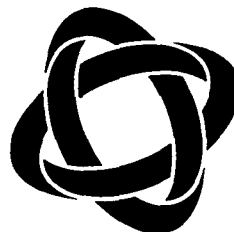
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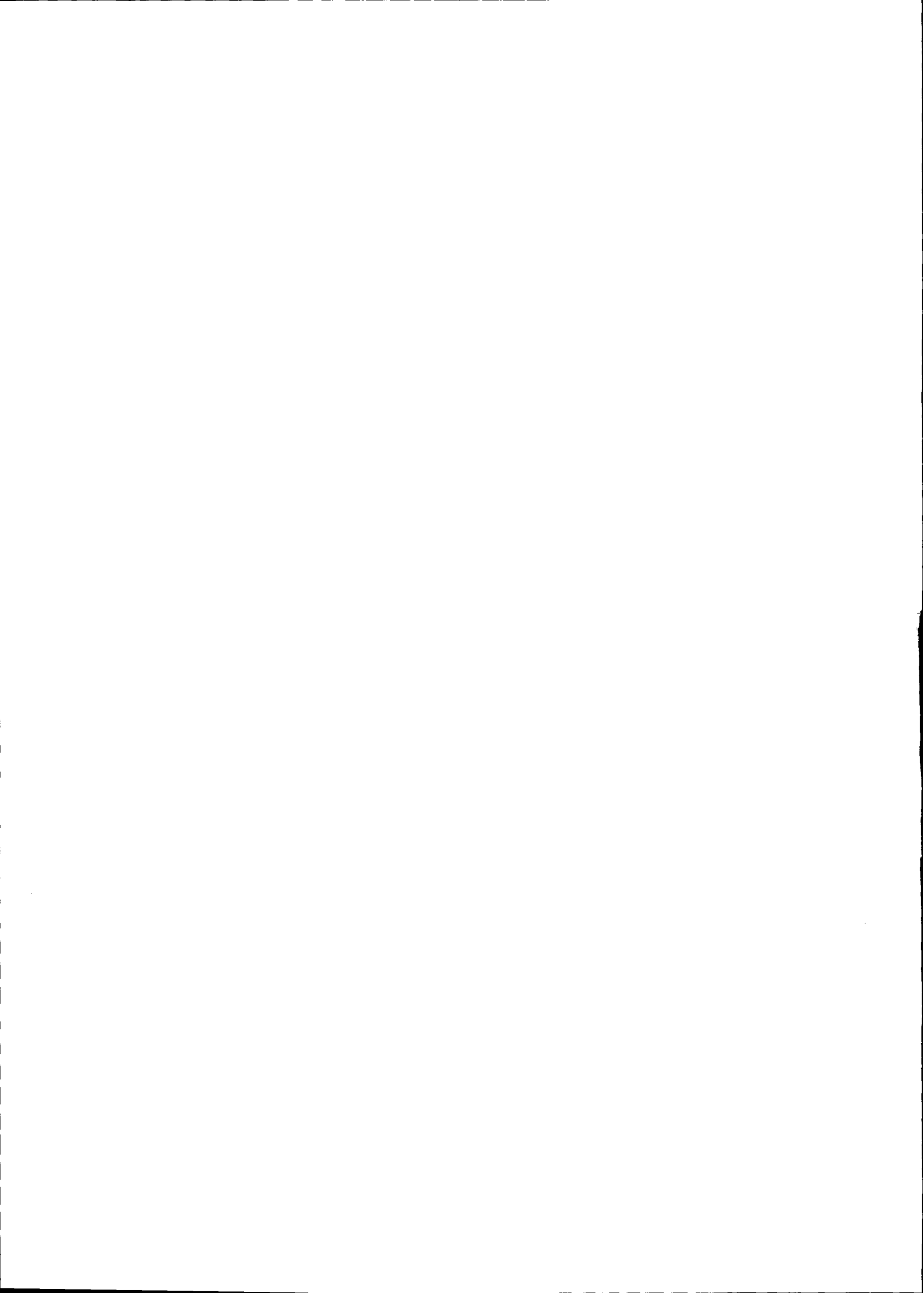
**EFFECTS OF HYDROGEN COMBUSTION
ON FISSION PRODUCTS AND AEROSOLS**

Technical Note by a Group of Experts

February 1993



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



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ON FISSION PRODUCTS AND AEROSOLS**

TECHNICAL NOTE BY A GROUP OF EXPERTS

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ABSTRACT

A hydrogen combustion could perturb the iodine chemistry and change the iodine volatility, mainly by enhancing the oxidation of suspended cesium iodide aerosols or causing revolatilization of volatile forms of iodine adsorbed on surfaces. Recent work at Sandia, Oak Ridge and Whiteshell have shown that molecular iodine can be formed from these aerosols during a hydrogen combustion under dry conditions, but that steam strongly inhibits its production. The results available, including the results of tests with steam present, are not really understood. Also the potential role of the flame front in revolatilizing iodine adsorbed on walls has not been investigated.

The presence of iodine or suspended aerosols could also affect the combustion process, but very little can be said about these potential effects. Iodine compounds are expected to act as chemical flame inhibitors, but their concentrations would almost certainly be too small to have any effect. The aerosols could also act as physical flame enhancers by promoting turbulence at the microscopic level. It is also possible that, if they were combustible, they could contribute to the combustion. Of course, cesium iodide is not particularly combustible.

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1. INTRODUCTION

This report summarizes the current knowledge of ways by which hydrogen combustion could affect iodine speciation and volatility in containment during and following an accident. A hydrogen combustion could potentially perturb the iodine chemistry and change iodine volatility, mainly by enhancing the oxidation of suspended cesium iodide aerosols or causing revolatilization of volatile forms of iodine adsorbed on surfaces. On the other hand, the presence of iodine or suspended aerosols could also affect the combustion process. These aspects of the possible interaction of hydrogen combustion and iodine volatility will be considered separately in the following sections.

2. HYDROGEN COMBUSTION EFFECTS ON IODINE CHEMISTRY

Some information exists on the way hydrogen combustion could affect iodine chemistry. If an accident occurs in a water cooled reactor, iodine is expected to be released into the containment largely as aerosols containing cesium iodide. Thus iodine transport immediately after the accident will be mostly by aerosol agglomeration and settling. However if a hydrogen combustion occurred soon after an accident, the cesium iodide in the aerosols could be converted quickly into more volatile forms of iodine, such as molecular iodine. Intermediate-scale experiments to examine this possible effect have been carried out in a meter-sized vessel at Sandia National Laboratories (SNL). These experiments were specifically intended to examine the effects of hydrogen combustion on the oxidation of suspended cesium iodide aerosols under dry conditions. Nelson et al. [1] demonstrated that significant oxidation of cesium iodide to iodine could occur. Indeed, using a CsI/Al₂O₃ co-aerosol mixture, they found that the yield of I₂ increased linearly with increasing hydrogen concentration; up to 75% conversion to I₂ was observed with 29% H₂ - 61% air mixtures, which correspond to stoichiometric mixtures.

At Oak Ridge National Laboratory (ORNL), Brown et al. [2] conducted a series of bench-scale experiments in which various iodine species were introduced into standing hydrogen flames. Tests with cesium iodide revealed that up to 73% of the added cesium iodide could be oxidized to I₂, provided that the flame temperature exceeded approximately 1400 K. Furthermore, the highest recoveries of I₂ were observed in tests with the largest H₂O:CsI ratios. These results were rationalized in terms of vapourization and gas phase thermal decomposition of CsI:



The steam (H₂O) effect could be explained by thermodynamics, since high H₂O concentrations would shift Equilibrium (1) to the right, in favour of cesium iodide decomposition. Brown et al. [2] also showed that iodate is formed in standing hydrogen flames, and could account for over 1/3 of the total iodine. In addition, a limited number of tests with HI and organic iodides revealed elemental iodine as the predominant product of reaction.

The recent experimental studies at Whiteshell, conducted as part of the Advanced Containment Experiments (ACE) program, examined the effects of steam on cesium iodide oxidation during hydrogen combustion in a 2.3 m diameter combustion testing apparatus, the Containment Test Facility [3]. Both dry and humid conditions were investigated. These intermediate-scale tests verified

that significant oxidation of suspended cesium iodide to gaseous iodine (15%) occurs during combustion of dry stoichiometric hydrogen-air mixtures. However, this work also revealed that only 10% steam prevents significant production of I_2 .

These findings could possibly be rationalized in terms of the formation of a water film on the aerosol surface when steam is present. Because the aerosol is in contact with the combustion front only for a limited period of time, the sorbed water might not be fully vapourized. The water film might then protect the cesium iodide aerosol from the high temperatures (i.e., 2700 K) and high radical concentrations (ie., $OH\cdot$) associated with the combustion front, preventing cesium iodide oxidation. It should be noted, however, that recent results from the Winfrith laboratory (B.R. Bowsher and M.S. Newland, private communication) have put into question the hygroscopic nature of cesium iodide at elevated temperatures. This puts into question the above interpretation of the mitigating effect of steam and makes it clear that further studies are required.

There are numerous outstanding issues regarding hydrogen combustion effects on iodine behaviour within containment. For example, the observation that 10 vol% steam effectively prevents I_2 formation should be kept in context. The ACE results [3] demonstrated the effect of steam only at a single steam concentration; no information on what happens at either lower or higher steam concentrations is available. Furthermore, the work of Brown et al. [2] suggests that cesium iodide oxidation increases with increasing $H_2O:CsI$ ratios. This needs to be tested in a systematic manner over a wide range of steam concentration.

The effects of aerosol concentration should also be addressed. The ACE tests were conducted at a single cesium iodide aerosol concentration as well. Furthermore, these tests were conducted with a very high concentration of suspended cesium iodide aerosols. The concentration range studied should include the concentration expected under accident conditions.

The effect of co-aerosols needs to be addressed. The ACE program used very high purity cesium iodide (99.999%). Alternatively, the SNL work used a mixture of cesium iodide and aluminum oxide. The yields of I_2 in the two programs were also significantly different (75% vs 15%). It is conceivable that this difference is due to the co-aerosol. In any event, in an actual accident, cesium iodide released into containment would be associated with various types of co-aerosol material.

The aerosols used in the SNL work had a particle size of approximately 50 microns. The ACE program used 10 micron particle size cesium iodide. In the early stages of an accident, large concentrations of sub-micron particles would be expected. Tests with different particle size aerosols should be undertaken.

The work completed to date has focussed on suspended aerosols. However, at later stages of an accident, the aerosols will be primarily deposited on surfaces. The combustion may effect the physical resuspension of the aerosol material. In one of the aborted ACE tests, the cesium iodide aerosol was prematurely dispersed. By the time combustion was initiated, most of the aerosol had settled onto the vessel surfaces. Nevertheless, elemental iodine was still detected.

Hydrogen combustion may also influence iodine speciation in a beneficial way. For example, gas phase I_2 and organic iodides, formed thermally or radiolytically within containment, could be converted in part to non-volatile iodine species. Some work on this topic was undertaken by Brown et al. [2]; however, additional work, including intermediate-scale experiments, should be undertaken.

3. REVOLATILIZATION OF IODINE

A hydrogen combustion has the potential to cause revolatilization of iodine adsorbed on surfaces. The tests in the Radioiodine Test Facility have shown that organic coatings are good sinks for iodine and that an appreciable fraction of the iodine inventory can be immobilized there. This would normally be considered desirable since the surfaces in contact with the gas phase then serve as "sinks" for iodine. However, the tests carried out in the Containment Test Facility, described above, revealed that dramatic scorching of even high temperature epoxy surfaces could occur during hydrogen deflagrations. Thus the high flame temperatures and reactive conditions associated with the combustion could greatly enhance the revolatilization of adsorbed iodine. To the best of our knowledge, this revolatilization has not yet been studied at any laboratory.

4. HYDROGEN COMBUSTION AEROSOL INTERACTIONS

In combustion, chemical and transport processes are closely coupled. While combustion processes are essentially chemical reactions with net heat evolution, conditions for reaction at the molecular level are preceded by physical processes governing the motion of reactants into the reaction zone. Thus, aerosols and fission products may affect combustion through chemical or physical interactions. One other category of effect is where the aerosol itself is flammable and present in large quantities, called hybrid combustion.

4.1 Chemical Effects

Reactive airborne fission products can chemically affect combustion behaviour to the extent that they contribute or compete for chain carriers in the chain branching reaction mechanism. Combustion behaviour likely to be affected include burning velocity, flammability limits and ignition. The inhibiting effect on hydrocarbon combustion by halogens (I_2 , Br_2 , Cl_2) and halogenated compounds (CH_3I , CF_3 , Br , etc.) has been well-studied [4]. The mechanisms for the observed effects involve predominantly interactions with the hydrogen atom and thus should be applicable to hydrogen flames as well.

Molecular and organic halogens (i.e., I_2 , CH_3I) react with radicals in the flame to yield halogen atoms. Halogen atoms act to catalyse the recombination of hydrogen atoms, further reducing the radical pool and lowering the rate of chain branching. Iodine atoms are the most effective chemical inhibitors of combustion, relative to bromine and chlorine atoms. The presence of 1% halogenated compound produces a significant suppression of burning velocity in hydrocarbon flames. Comparable inhibition may be expected to occur in hydrogen flames. However, in containment, iodine concentrations are unlikely to be as high as 1%, so the effect on burning velocity will probably be slight. Potentially greater effects may be observed in ignition and flammability behaviour where concentrations of chain carriers are crucial.

4.2 Physical Effects

Suspended aerosols (solid or liquid) in the unburnt gas ahead of the flame can produce fine-scale turbulence in the unburnt gas flow which increases heat and mass transfer and thus, the local burning velocity. The magnitude of the effect is dependent on the size and the density (concentration) of the aerosols. The smaller the aerosol particles, the greater is the particle/gas flow fidelity and the smaller the effect. On the other hand, the suspended aerosol mass offers a heat sink which can act to reduce the final peak combustion pressure, particularly in the case of water aerosols where heat of evaporation comes into play. Significant reductions in flame temperatures (and peak pressures) are achieved from evaporation at droplet concentrations $>0.05\%$ of the volume. These effects are well-documented from studies of fogs and sprays as a means of combustion suppression [5].

4.3 Hybrid Combustion

Fission products or aerosols may, themselves, be flammable and undergo heat-releasing oxidation reactions. Relevant studies have been done in mining industries where coal dust and natural gas may burn together [6]. With regard to nuclear containments, a study was carried out at Sandia [1] where dry, cold aerosols were injected in large quantities into flammable H_2 -air volumes. Aerosols in a reduced state (metallic iron, iodide) and sufficiently concentrated ($>100 \text{ g/m}^3$) were found to act as additional fuel and increase the vigour of the burn. Aerosols in a fully oxidized state (metal oxides) produced only minor changes in combustion behaviour and the aerosols were unchanged by the burn.

Steam was not present in these studies but is likely to affect the observed behaviour. As noted above, in the ACE experiments [3] at Whiteshell there were observations of significantly different behaviour for cesium iodide oxidation in dry and humid atmospheres. A review of severe accident scenarios to determine amounts of combustible aerosol that could possibly arise is required before hybrid burns are seriously considered.

5. SUMMARY

A hydrogen combustion event could perturb iodine chemistry and change the iodine volatility, mainly by enhancing the oxidation of suspended cesium iodide aerosols or causing revolatilization of volatile forms of iodine adsorbed on surfaces. While recent work at SNL, ORNL and Whiteshell have added appreciably to our general knowledge of the effects of hydrogen combustion on iodine behaviour, there remain many uncertainties that must be addressed before iodine chemistry and combustion phenomena within containment are adequately understood. These include aerosol concentration, aerosol size, co-aerosol effects and humidity. Moreover, observations made to date, including the humidity tests, are not really understood, even at the most rudimentary level. The role of the flame front in revolatilizing iodine adsorbed on walls has not been investigated.

The presence of iodine or suspended aerosols could also affect the combustion process, but even less can be said with certainty about these potential effects. Iodine compounds are expected to act as chemical flame

inhibitors, but their concentration would be too small to have any effect. The aerosols could act as physical flame accelerators by promoting turbulence at the microscopic level. Also, if they were combustible, they could contribute directly to the combustion.

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Appendix

List of Members of the CSNI-PWG4 Task Group on
Fission Product Phenomena in the Containment (FPC)
(April 1992)

| | |
|---|---|
| Austria | Dr. Gert <u>Sdouz</u> (Seibersdorf) |
| Belgium | Mr. Albert <u>Delbrassine</u> (CEN/SCK Mol) |
| Canada | Dr. Norman H. <u>Sagert</u> (AECL/WNRE) * |
| Finland | Dr. Jorma <u>Jokiniemi</u> (VTT) |
| France | Dr. Jean-Pierre <u>L'Hériteau</u> (CEA/IPSN) |
| Germany | Dr. Werner <u>Schöck</u> (KfK) Dr. Eugen <u>Schrödl</u> (GRS) |
| Italy | Dr. Giancarlo <u>Sandrelli</u> (ENEL/CRTN) |
| Japan | Mr. Kikuo <u>Akagane</u> (NUPEC) Dr. Kunihisa <u>Soda</u> (JAERI) - <u>Chairman</u> Dr. Jun <u>Sugimoto</u> (JAERI) |
| The Netherlands | Mr. Johan <u>Kanij</u> (KEMA) Mr. Simon <u>Spoelstra</u> (ECN) |
| Sweden | Mr. Kjell O. <u>Johansson</u> (Studsvik) |
| Switzerland | Mr. Salih <u>Güntay</u> (PSI) Dr. Günter <u>Prohaska</u> (HSK) |
| United Kingdom | Dr. Neil <u>Ketchell</u> (AEA Technology/SRD) Dr. Paul <u>Smith</u> (AEA Technology/WTC) |
| United States | Dr. Dana A. <u>Powers</u> (Sandia) |
| Commission of the European Communities | Mr. Enzo <u>Della Loggia</u> (DG XII) Mr. Iain <u>Shepherd</u> (JRC Ispra) |
| UNIPEDE | Mr. Michel <u>Lambert</u> (EDF/SEPTEN) |

OECD Nuclear Energy Agency:

Dr. Jacques Royen - Secretary

* Dr. Sagert prepared the successive versions of the draft of this report.

Annex

O E C D

The Convention establishing the Organisation for Economic Co-operation and Development (OECD) was signed on 14th December 1960.

Pursuant to article 1 of the Convention, the OECD shall promote policies designed:

- to achieve the highest sustainable economic growth and employment and a rising standard of living in Member countries, while maintaining financial stability, and this to contribute to the development of the world economy;
- to contribute to sound economic expansion in Member as well as non-member countries in the process of economic development; and
- to contribute to the expansion of world trade on a multilateral, non-discriminatory basis in accordance with international obligations.

The current Signatories of the Convention are Australia, Austria, Belgium, Canada, Denmark, Finland, France, the Federal Republic of Germany, Greece, Iceland, Ireland, Italy, Japan, Luxembourg, the Netherlands, New Zealand, Norway, Portugal, Spain, Sweden, Switzerland, Turkey, the United Kingdom and the United States.

N E A

The OECD Nuclear Energy Agency (NEA) now groups all the European Member countries of OECD and Australia, Canada, Japan and the United States. The Commission of the European Communities takes part in the work of the Agency.

The primary objectives of NEA are to promote co-operation between its Member governments on the safety and regulatory aspects of nuclear development, and on assessing the future role of nuclear energy as a contributor to economic progress.

NEA works in close collaboration with the International Atomic Energy Agency, with which it has concluded a Co-operation Agreement, as well as with other international organisations in the nuclear field.

C S N I

The NEA Committee on the Safety of Nuclear Installations (CSNI) is an international committee made up of scientists and engineers. It was set up in 1973 to develop and coordinate the activities of the OECD Nuclear Energy Agency concerning the technical aspects of the design, construction and operation of nuclear installations insofar as they affect the safety of such installations. The Committee's purpose is to foster international co-operation in nuclear safety amongst the OECD Member countries.

CSNI is sponsoring several Senior Groups of Experts and Principal Working Groups (PWG's). PWG4 is dealing with the confinement of accidental radioactive releases.