SUMMARY

At the invitation of the British Nuclear Energy Society (BNES) the IAEA convened the seminar/workshop on nuclear graphite waste management as a part of the Technical Committee meeting (TCM) on Characterization, Treatment and Conditioning of Radioactive Graphite from Nuclear Power Plants. The seminar was held on 18–20 October 1999 in Manchester, United Kingdom and was attended by more than 55 participants from 11 countries (Austria, Japan, Russia, Ukraine, France, Germany, Spain, the United Kingdom, Lithuania, Indonesia, and the United States of America). Twenty technical papers were presented and discussed in five sessions covering various aspects of radioactive graphite waste management. Practical approaches to the solution of particular technical problems were demonstrated during the technical visit to the Sellafield site on 20 October.

The seminar was followed up by a technical meeting attended by 11 participants nominated by the Member States. Information presented at the seminar was further reviewed and selected parts were incorporated in a draft technical document on characterization, treatment and conditioning of radioactive graphite from nuclear power plants.

BACKGROUND

Graphite has been used as a moderator and reflector of neutrons in more than 100 nuclear power plants as well as many experimental reactors and plutonium production reactors in various countries. Graphite is also used for fuel sleeves and other components, which are disposed of during operation and in some cases the volume of the graphite involved is of the same order as the core itself. Considering that the core of a typical graphite moderated reactor may contain 2000 tonnes of graphite, the volumes involved are considerable.

Most of the older graphite moderated reactors are already shut down and therefore decommissioning planning and preparation represents a very serious matter. Radioactive graphite dismantling, handling, conditioning and disposal are a common part of the decommissioning activities.

The radioactive graphite coming from nuclear installations has different characteristics than other radioactive waste due to its physical and chemical properties and also because of the presence of tritium and carbon-14. Even after many years of irradiation, graphite retains most of the good mechanical properties and is relatively insoluble and not otherwise particularly chemically reactive. It appears therefore to fulfil most of the general requirements for a solid radioactive waste form suitable for disposal. However, the evaluation of the radioactivity inventory of graphite moderators and other details of graphite used in nuclear reactors show that this graphite cannot be accepted by existing disposal sites without particular conditioning.

Depending on the graphite source (moderator, fuel compartments details-sleeves), various radionuclides are present — mainly tritium, ^{14}C, but also corrosion/activation products (^{57}Co, ^{60}Co; ^{54}Mn; ^{59}Ni, ^{63}Ni; ^{22}Na), fission products (^{134}Cs, ^{137}Cs; ^{90}Sr; ^{152}Eu, ^{154}Eu, ^{155}Eu; ^{144}Ce) and small amounts of uranium and transuranium elements (^{238}Pu, ^{239}Pu; ^{241}Am, ^{243}Am).

The graphite in some of the experimental and plutonium production low temperature reactors contains a considerable amount of stored Wigner energy. Unexpected release of Wigner energy, mainly in the older graphite moderated reactors, particularly those built to produce plutonium, caused several incidents, also connected sometimes with fuel failure. This has led, in some cases, to considerable contamination of the graphite by fission products. Potential risk connected with accumulated Wigner energy is one of the main factors which has to be taken into account during graphite waste processing and disposal.

Different options have been studied for management of the radioactive graphite, but the final and generally accepted solution for its conditioning and/or disposal has not been decided yet.

Disposal options proposed are near surface repositories and also deep geological formations. Sea disposal is no longer an acceptable option.

PURPOSE OF THE SEMINAR

The seminar covered radioactive graphite characterisation, the effect of irradiation on graphite components, Wigner energy, radioactive graphite waste treatment, conditioning, interim storage and long term disposal options.

The purpose of the seminar was to bring together the specialists dealing with various aspects of radioactive graphite waste management to exchange and review information on the decommissioning, characterization, processing and disposal of irradiated graphite from reactor cores and other graphite waste associated with reactor operation. Twenty presentations were made with an open discussion following each paper. Selected information will also be reflected in a technical publication on characterization, treatment and conditioning of radioactive graphite from nuclear power plants

SUMMARY OF PRESENTATIONS

General issues relating to radioactive graphite waste management

B. Marsden, in his introductory presentation, outlined the main technical and technological factors applying to the management of radioactive graphite waste.

On the negative side there are:

- The large volumes of radioactive graphite waste involved: about 60 000 tonnes in the UK, 50 000 tonnes in the former Soviet Union, similar amounts in France and in the USA as well as graphite waste from reactors in Spain, Italy, Japan, the Democratic Peoples Republic of Korea and China.
- The significant quantities of the long lived isotope Carbon-14, as well as significant amounts of Tritium and other radionuclides contained within the graphite waste.
- There are two main sources of graphite waste, the reactor cores themselves, and also other graphite associated with the fuel or fuel channels that is stored in silos and other shallow repositories. This latter waste, for a particular reactor, can amount to a similar volume to the reactor core. Moreover, this waste is usually more contaminated, very often by fission products and transuranium elements.

- In some special cases, such as Windscale Pile 1 and some of the graphite waste stores in Siberian Plutonium production reactors, immediate action is necessary to dismantle/empty the storage facilities due to the presence of damaged fuel in the store and/or due to the deterioration of the storage facility.

On the positive side are:

- Graphite is an inert stable material that maintains its good mechanical properties in adverse conditions over many years. Therefore, in many cases, the "safe storage" concept can be used to allow the high levels of radioactivity after reactor shut down to decay.
- The technology exists to deal with the waste.
- The technology used to dispose of irradiated graphite waste in a safe and efficient way is available and need not involve a high level of technological skill.

However, the location and construction of near surface or deep geological waste repositories requires political support that is out of the hands of the nuclear industry.

In the first paper, Wickham and Neighbour took a fresh look at the technical as well as socio-political aspects of radioactive graphite waste management, covering both the history that has led to the present position and possible ways forward. The paper was focused on the various final solutions of the "graphite problem" from deep-sea disposal, through incineration and subsequent disposal of the residual ash, to the disposal of treated graphite in a deep geological formation. A review was given of the methods for treatment and conditioning of radioactive graphite waste that have been considered and investigated. The public response to proposals for deep-sea disposal, the location of near surface disposal sites and the perceived public response that may apply to incineration, are covered. Finally, the paper puts forward the proposal that the case for graphite processing and disposal should be looked at again from a purely scientific basis, based on detailed risk assessment of various options.

Wigner energy

Several papers were presented covering the management of irradiated graphite waste containing stored energy[1]. Whilst these papers were relating to the decommissioning of the Windscale Piles and other graphite associated with these reactors, the methods described will find application when considering decommissioning of BEPO at Harwell, G1 in France and some other facilities elsewhere. The papers covered the characterisation of waste containing stored energy, methods of annealing out stored energy, tritium releases during the annealing process and methods of modelling the release of stored energy during packaging, within the storage and disposal and in other circumstances.

P. Minshall described a computer model of stored energy release in graphite based on a chemical rate equation. This model was fitted to experimental data from samples taken from Windscale Piles 1 and 2. He demonstrated the use of the model by assessing experiments carried out on Windscale graphite subject to various thermal cycles.

[1] Stored (or Wigner) energy is potential energy caused by irradiating graphite at low irradiation temperatures. If the temperature of irradiation is sufficiently low (below 150^{o}C) this energy can be accidentally released in a self sustaining reaction raising the graphite temperature to around 400^{o}C in certain circumstances.

A paper followed this presentation (R.M. Guppy, J. McCarthy and S.J. Wisbey) describing the use of this model for assessing the behaviour of graphite containing stored energy in conditions of a deep geological waste repository. The purpose is to assess the possibility of stored energy release leading to degradation of the waste form or to a reduction in the ability of barriers and back-fill materials to control chemical conditions of the disposal site environment. The model included heat from the host rock, radioactive decay, corrosion processes and heat from the curing of back-fill materials. The same model has also been used to assess the behaviour of waste packages containing graphite waste during grouting and possible fire accidents to packages containing graphite waste during transport.

M. Wise outlined the graphite-moderated reactors, for whose decommissioning UKAEA is responsible. These include GLEEP, BEPO, the Windscale Piles and WAGR. In addition to the moderator of these reactors there is also graphite associated with reflectors, thermal shields and thermal columns in DFR, DIDO, PLUTO and DMTR. The paper describes in detail the graphite waste associated with all of these reactors and outlines possible methods of dealing with each particular category of this waste, including the possibility of incineration for some low level graphite waste. The problems associated with graphite dust during packaging and the possibility of galvanic corrosion of the waste package are also described. Among all these reactors, graphite from Windscale Pile 1 and 2 and BEPO contain significant amounts of stored (Wigner) energy.

The methodologies and facilities required to anneal out Wigner energy were described in two papers. The first dealt with the methods investigated to anneal the Windscale Pile graphite. The proposal is to heat the graphite to 250^{o}C in special ovens located near to Windscale Pile 1. Three heating methods were investigated; convection, radiation and induction. The induction heating was found to be the better option, due to the direct heating into the bulk of the graphite. As most of the heat is generated in the graphite itself, the oven and heating equipment can be quickly cooled. This allowed the desired throughput using the minimum number of annealing ovens. Assessment has also been made into the emission of tritium during the annealing process. Analysis showed the tritium content to be about 100 kBq/g. The annealing process described above, allows a heating time of approximately 20 minutes at around 300 to 400^{o}C. Therefore the tritium release was measured on graphite samples between 150 and 700^{o}C. Below 500^{o}C less than 1% of the total tritium content was released mainly as tritiated water. At 700^{o}C the release is mainly tritiated hydrogen.

Effect of irradiation on graphite components and irradiated graphite characterization

Besides the risk of stored (Wigner) energy, irradiation of graphite components in the reactor core can cause changes of several graphite properties. Another unavoidable effect of graphite utilization in a reactor is increased radioactivity of graphite parts. Graphite, impurities and admissions in graphite, as well as blanket gas, are activated in a reactor core. Graphite components are very often contaminated by fission products from damaged fuel elements or by activated corrosion products from reactor parts.

The results of an extensive investigation of a whole channel of graphite blocks being removed from the RBMK-1000 reactor at Leningrad NPP Unit 3 after 18 years of operation was described in a paper of O.K. Chugunov. This is a unique undertaking for a large graphite moderated reactor and will provide important information on the build-up of stresses and deformations in graphite components. Measurements were made of the physical property changes as well as the isotopic content of samples taken from these blocks. The blocks were found to have shrunk about 2% in the axial direction and 1% in the radial direction and the elastic modulus had increased about 40%. Investigations were made of gas release under gamma irradiation (at a dose rate of 80 rad/s). It was shown that gas output from irradiated graphite increased about 10-11 times. Chromatographic analyses of the gas showed the main constituents to be H_2-19%, N_2-36% and CO_2-40%. Leaching tests showed that the total output of Cs^{137} in solution after 90 days is about 6.4×10^3 Bq.

A paper was presented by P. Poskas from the Lithuanian Energy Institute on the thermal strain measurements in graphite using electronic speckle pattern interferometry. This method has been developed for surveillance of the graphite blocks during the safe storage period of decommissioning. It uses laser light which reflects off the object surface to give an electronic speckle pattern and is a contact-less method to make strain measurements on the reactor components.

A very interesting paper of R. Takahashi et al. describes the relationship between leaching of ^{14}C and the graphite morphology. Nuclear graphite is a polycrystalline structure in which the crystals are well formed. They investigated how the main precursor for carbon-14, Nitrogen, was located in the graphite microstructure. The main concentration of nitrogen (and hence ^{14}C) is shown to be weakly located at the crystal surface. However, they showed that the bulk of ^{14}C located in the matrix of the graphite crystallite was quite stable and only the ^{14}C located on the crystallite surface could be easily released by leaching.

B. Bisplinghoff et al. reported on the radiochemical characteristics of the shut down German AVR prototype pebble bed reactor. Two types of carbon material were used in this reactor. Graphite blocks formed the reflector and carbon blocks (non-graphitised carbon stock) was used as an insulation material. The method of analysing the samples for ^{14}C, ^{3}H and ^{36}Cl was described. Levels of Tritium were found to be approximately 40 MBq/g in the carbon bricks and 2 MBq/g for graphite. Carbon-14 levels were found to be 9 MBq/g for carbon bricks and 100 kBq/g for graphite. The carbon bricks were found to contain 5 MBq/g of ^{60}Co and 3 MBq/g of ^{55}Fe, with much lower levels of these two isotopes being found in the graphite. The reason for this is most probably due to the carbon being heat treated at a much lower temperature than the graphite (800°C compared with ~3000°C for the graphite). In addition the graphite may have been purified in a halogen gas at around 2400°C. This example shows the importance of understanding and controlling the chemical composition of the impurities in carbon insulation materials for new reactor designs.

Two papers covered the issues relating to the light water-cooled graphite moderated plutonium production reactors in the former Soviet Union. Some of them have been subject to fuel channel tube and fuel failures, which have released uranium and fission products into the graphite stack. Thus the role of these events in the contamination of the entire stack is of interest. Also of interest is how the activation of the nitrogen blanket, which surrounded the graphite core to limit graphite oxidation, may have contributed to the contamination. Several hundred samples from the shut down Siberian production reactors EI-2 and I-1 have been taken and measurements have been performed of long lived β-emitters (such as ^{14}C and ^{3}H), actinides, fission products and ^{60}Co.

Carbon-14 was found to be the dominant contributor to the graphite activity. The distribution of this isotope was found to approximately follow the thermal neutron flux. Within a graphite block the distribution was found to be approximately uniform. Comparisons were made with measurements of ^{14}C from the Hanford DR. These showed higher levels of ^{14}C, probably due to the use of CO_2 as a blanket in the DR reactor instead of nitrogen.

Tritium in the Russian reactors was about 50 times less than in the DR reactor. This was attributed to tritium being carried away in "wet" events by the water vapour and cover gas during these events, which often occurred in the Russian reactors. Cobalt-60 within the graphite blocks due to activation of impurities, or on the surface of graphite blocks due to contamination, was found to be fairly uniform throughout the stack. Actinides were present as surface contamination. It was proposed that a simple measurement of ^{137}Cs should be used to sort graphite blocks before processing.

Chorine-36, arising from activation of residual chlorine used in the graphite purification process, represents another significant contaminant of radioactive waste graphite. This isotope is important as it is long lived and poorly retarded by geological barriers. A paper prepared by UK NIREX, outlined a recent extensive work programme they undertook to investigate the impact of ^{36}Cl on the repository design and packaging requirements. The assessments were based on activation calculations rather than measurements due to the difficulty the latter approach would pose. Over 458 graphite samples were measured to obtain a probability density function for the mean chlorine concentration. Studies showed that a significant fraction of chlorine is released from graphite during irradiation both as a precursor and activated. As the packages will not be able to retain their integrity for a comparable time to the half-life of ^{36}Cl the radiological risk is based on the dilution and long return times for the proposed repository.

Radioactive graphite dismantling, processing and disposal

The most significant number of graphite moderated reactors is intended to be decommissioned in the United Kingdom. Windscale AGR is being dismantled to a green field site as a UK demonstration project. However, stored energy in this reactor graphite is of no concern due to the high irradiation temperature.

G. Holt (BNFL, Magnox Electric) gave a presentation covering the 26 Magnox reactors in the UK. Six of these reactors are now shut down and being decommissioned. In addition there are various graphite wastes associated with the fuel (fuel sleeves and struts). The decommissioning of the reactors themselves is based on a safestore strategy. A maximum period of 135 years after shutdown has been calculated for the activity to fall to a stabilised level. After this period it is considered that there is nothing to gain from any further period of waiting before dismantling. However, it is likely that the safe storage period will be less than this.

Intermediate level graphite waste from the UKAEA reactors is to be disposed of in an UK deep waste repository. However, as a repository is not available at present, graphite from Pile 1 and its associated waste store and graphite from B41 are to be suitably packaged and kept in an intermediate store until the deep geological waste repository becomes available.

One of the most prominent graphite decommissioning projects at present is the Tokai Magnox power station in Japan. A paper from NUPEC described some of the developments in graphite waste treatments directed at this project. Tokai, Japan's first power producing nuclear power plant, was operated over a long period from 1966 to 1998. In addition to the graphite waste in the core and reflector, there is also a large amount of graphite fuel sleeve waste in store on the site. It is envisaged that there will be a relatively short period of safe storage, 5 to 10 years, compared to 135 years, which is the maximum storage period under consideration in the UK. The reason for this short storage period is to make the site available for the construction of a new nuclear power station. Assessments have been made to investigate risks of possible combustion of graphite dust during decommissioning along with methods of dust collection. Various methods of collecting the ^{14}C off-gas using absorption in zeolites were also investigated. The efficient packaging of the graphite as it is removed from the core and investigation of cementation for packaging are of particular interest.

There are around 30 000 graphite bricks to be removed from the reactor in Tokai, in columns 10 layers high, each brick weighing some 50 to 70 kg. To remove these bricks efficiently M. Shirakawa et al. investigated a possibility of grasping several bricks at the same time. The cost of disposal of the graphite will account for a considerable amount of the decommissioning costs. Thus the importance of packing densities and the possibility of cutting components into convenient shapes to facilitate efficient packing were discussed in some detail.

The problems related to the cutting of irradiated graphite components were discussed also by D. Holland et al. Thermal cutting, wet jet stream, mechanical saw, plasma, drilling and hydraulic splitting are being evaluated as part of a research programme to deal with graphite waste from the German nuclear industry. This project has just started and the paper covered the initial progress.

A novel method of processing graphite waste was presented by J.B. Mason and D. Bradbury. This methodology involved the use of pyrolysis/steam reforming followed by off-gas control. The cleaning system is based on experience gained with similar way of processing spent ion exchange resins. The exhaust gas could be solidified in the form of calcium carbonate which could be used to fill voids in other radioactive waste. It was suggested that the process could either be used to process graphite removed from the core or even applied to gasify graphite waste within the core.

CONCLUSIONS

The recent status and perspectives of radioactive graphite management were discussed during presentations as well as in a round table discussion among the seminar participants. Essential results from the discussion are reflected in the following conclusions:

- Technologies and technological knowledge are available for safe and sound management of radioactive graphite waste. Nevertheless, existing processing technologies are based mostly on isolation (packaging) of radioactive graphite from the environment and they are not able to provide for a significant volume reduction.
- Incineration is only industrial technology, which could be characterized by notable volume reduction. Nevertheless, due to contamination of waste graphite by Carbon-14 and Tritium, incineration facilities need to be equipped by an efficient air filtration system, generating a considerable volume of secondary radioactive waste. Another option, tested recently at the pilot plant level, is steam reforming of graphite, using modified technology developed originally for processing of spent ion exchange resins.
- Considering good mechanical properties and relatively low leaching rates of radionuclides from graphite waste, safe storage of bulk pieces of radioactive graphite

waste (moderator, reflector, etc.) represents a reasonable option to await a final decision on graphite waste management.

- A special category of radioactive graphite waste is fuel sleeves and other reactor core components from former plutonium production reactors, often heavily contaminated by fission products, which are stored in silos not assuring proper isolation from the environment. Recovery, conditioning or transfer into safer storage facilities are the most urgent problems in the United Kingdom as well as in the Russian Federation.
- Radioactive graphite waste can contain stored (Wigner) energy. This fact and corresponding measures must always be considered in the planning of each step of graphite waste management.