PYROLYSIS AND ITS POTENTIAL USE IN NUCLEAR GRAPHITE DISPOSAL

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Abstract. Graphite is used as a moderator material in a number of nuclear reactor designs, such as MAGNOX and AGR gas cooled reactors in the United Kingdom and the RBMK design in Russia. During construction the moderator of the reactor is usually installed as an interlocking structure of graphite bricks. At the end of reactor life the graphite moderator, weighing typically 2,000 tonnes, is a radioactive waste which requires eventual management.

Radioactive graphite disposal options conventionally include:

- In-situ SAFESTORE for extended periods to permit manual disassembly of the graphite moderator through decay of short-lived radionuclides.
- Robotic or manual disassembly of the reactor core followed by disposal of the graphite blocks.
- Robotic or manual disassembly of the reactor core followed by incineration of the graphite and release of the resulting carbon dioxide

Studsvik, Inc. is a nuclear waste management and waste processing company organised to serve the US nuclear utility and government facilities. Studsvik's management and technical staff have a wealth of experience in processing liquid, slurry and solid low level radioactive waste using (amongst others) pyrolysis and steam reforming techniques. Bradtec is a UK company specialising in decontamination and waste management.

This paper describes the use of pyrolysis and steam reforming techniques to gasify graphite leading to a low volume off-gas product. This allows the following options/advantages.

- Safe release of any stored Wigner energy in the graphite
- The process can accept small pieces or a water-slurry of graphite, which enables the graphite to be removed from the reactor core by mechanical machining or water cutting techniques, applied remotely in the reactor fuel channels.
- In certain situations the process could be used to gasify the reactor moderator in-situ.
- The low volume of the off-gas product enables non-carbon radioactive impurities to be efficiently separated from the off-gas.
- The off-gas product can be discharged to atmosphere if permitted, or can be absorbed and converted to a low-activity carbonate solid product, which can be used as in-fill around other radioactive waste.

1. INTRODUCTION AND PROBLEM OVERVIEW

Graphite, which consists predominantly of the element carbon, is used as a moderator in a number of nuclear reactor designs, such as the MAGNOX and AGR gas cooled reactors in the United Kingdom and the RBMK design in Russia. During construction the moderator of the reactor is usually installed as an interlocking structure of graphite bricks. At the end of reactor life the graphite moderator, weighing typically about 2,000 tonnes, is a form of radioactive waste which requires eventual management. Graphite is a relatively stable chemical form of carbon, which is in many ways suitable for direct disposal without processing. However, after neutron irradiation the graphite will contain stored Wigner energy. The potential for release of this energy needs to be accommodated in any strategy which relies on disposing of the graphite in unprocessed form. Alternatively, processing the graphite before disposal can allow the safe release of any stored Wigner energy.

The graphite also contains significant quantities of radionuclides from neutron induced reactions, both in the graphite itself and in the minor impurities which it contains. The radioisotope content can conveniently be divided into two groups. Short lived isotopes (such as cobalt-60) make the graphite difficult to handle immediately after reactor shutdown but decay after a few tens of years. Long-lived isotopes (principally carbon-14) are of concern through the possibility of their discharge to the biosphere. Processing the graphite offers the opportunity to separate the majority of the graphite mass (carbon) from the short-lived radioisotopes. This in turn facilitates management of graphite waste shortly after the end of reactor life.

The potential future radiological impact of graphite is probably less serious than that of other radioactive wastes, but will be subject to regulatory attention under the principles of "ALARP" (As Low As Reasonably Practical). It is not necessarily obvious what management strategy will be optimum. If it is desired to contain the carbon-14 of the graphite for tens of thousands of years in order to avoid radiation exposure in the biosphere, the long term confinement of graphite presents interesting challenges, because of the innate potential of graphite to become converted to gaseous forms. In addition, for very long-term burial, potential intruder scenarios include the mining of buried graphite for use as fuel by future less sophisticated groups which would lead to potentially significant exposures.

On the other hand, it is not at all certain that the early deliberate release of the carbon-14 content of the moderator to the atmosphere would be radiologically unacceptable, since large amounts of this isotope are continuously and naturally formed in the atmosphere anyway. It is relatively simple to prove that, provided the release is carried out in a suitable manner, the radiation dose to any individual from this practice would be trivial. However, the collective radiation dose to all people integrated over thousands of years may be considerable. Whether release in this manner will be acceptable is heavily dependent on the evolving debate about the significance of large collective (but individually trivial) radiation doses. The risk of a significant future individual dose (eg by release or intrusion in long term disposal) might outweigh the significance of collective doses from immediate release. Disposal at sea would mitigate some concerns, because any released carbon-14 would be diluted into the seas' large inventory of carbon rather than the smaller atmospheric inventory. However, sea disposal is internationally considered unacceptable for political reasons. While the "concentrate and contain" philosophy is undoubtedly appropriate for most radioactive wastes, graphite is possibly a special case where release to atmosphere may be appropriate. If the graphite is to be dispersed in gaseous form in the atmosphere, it is essential to minimise the release of any non-carbon isotopes such as tritium, iron-55 and cobalt 60. This implies a requirement for the efficient gasification of the carbon and its separation from other radioactive residues.

Another potential option would be to react the carbon dioxide with calcium or magnesium oxide, hydroxide or metal to form a stable carbonate solid. The resultant solid would have greater volume than the original graphite. However, if this solid were pelletised, it could be used as void in-fill in grouting of other radioactive waste. A particularly interesting possibility at MAGNOX reactors is to use the Magnox fuel cladding or splitter waste as the source of magnesium for this option, thereby dealing with two radioactive wastes in one just one waste form. Carbon dioxide is already used in the processing of Magnox waste [I].

Because of its characteristics and the mass of graphite, the most common procedure to date for decommissioning of graphite moderated reactors is to "SAFESTORE" the reactor core in-situ for a period of tens of years following reactor shut-down. During this period short-lived radioisotopes decay sufficiently to allow eventual manual dismantling of the

graphite moderator. Most UK plans then assume that the graphite will be disposed of in its existing chemical form, with appropriate additional packaging to prevent degradation or release over the long period of carbon-14 decay.

Safe-store has certain negative consequences, since it implies a long-term financial liability, a visually intrusive structure that has no productive purpose, a requirement for continual surveillance and the requirement for a future generation (which gained no benefit from the original asset) to complete its eventual clearance. If the safe-store alternative is to be replaced by shorter term management, it is essential that technology exists for the economic early retrieval and processing of the graphite in a safe and radiologically acceptable manner.

2. OVERVIEW OF STUDSVIK, INC. AND BRADTEC DECON TECHNOLOGIES LTD

Studsvik, Inc. is a nuclear waste management and waste processing company organised to serve US nuclear utility and government facilities. Studsvik's management and technical staff have a wealth of experience in processing liquid, slurry and solid Low-Level Radioactive Wastes (LLRW). The following principal technologies are used: pyrolysis, steam reforming, vitrification, thermal treatment, incineration, offgas control systems, ion exchange, reverse osmosis, membrane separations, solidifications, metal melting, evaporation, transportation, packaging and burial of a wide range of LLRW streams.

Studsvik, Inc. is a subsidiary of Studsvik Holding AB, a Swedish nuclear services and waste management company located south of Stockholm, Sweden.

Bradtec is a UK company specialising in decontamination and waste management.

Studsvik, Inc. has completed construction, start-up testing, and has commenced commercial operation of a Low-Level Radioactive Waste (LLRW) processing facility in Erwin, Tennessee, USA. The Studsvik Processing Facility (SPF) has the capability to safely and efficiently receive and process a wide variety of solid and liquid LLRW streams including: ion exchange resins (IER), charcoal, graphite, sludge, oils, solvents, and cleaning solutions with contact radiation levels of up to 2.0 Sv/h (200 R/h). The licensed and heavily shielded SPF can receive and process over 10 tons of LLRW slurry feed per day, including liquid and solid LLRW's with high water and /or organic content. Figure 1 shows a view of the Studsvik Processing Facility.

The SPF employs the patented Thermal Organic Reduction (THOR ^{SM}) process [2], developed by Studsvik, which utilises pyrolysis/steam reforming technology. THOR ^{SM} reliably and safely processes a wide variety of LLRW's in a unique, moderate temperature, pyrolysis/reforming, fluidised bed treatment system. The THOR ^{SM} technology is suitable for processing hazardous, mixed and dry active LLRW (DAW) with appropriate licensing and waste feed modifications.

Operations have demonstrated consistent, reliable, robust operating characteristics with volume reductions up to 80:1 and weight reductions up to 100:1 when processing depleted, mixed bed, ion exchange resins with over 99.9% of all non-volatile radionuclides in the waste feed incorporated in the final solid residue product. Final reformed residue comprises a non-dispersible, granular solid suitable for long-term storage or direct burial in a qualified container. THOR ^{SM} effectively converts hexavalent chromium to non-hazardous trivalent chromium and can destroy/convert nitrates to nitrogen with over 99 percent efficiency in a single pass.

FIG. 1. Studsvik processing facility at Erwin, Tennessee, USA.

3. GRAPHITE PROCESSING OPTIONS WITH PYROLYSIS/STEAM REFORMING

In the pyrolysis/steam reforming process organic or carbon bearing materials are reduced through pyrolysis in the presence of insufficient or no oxygen to produce volatile gases and a fixed-carbon "char". In certain applications the char may then be further processed with steam to gasify the carbon content in the char according to the general reaction

$$C + H_20 \rightarrow CO + H_2$$

The steam reformation part of the process is the principal part for graphite treatment, since graphite only contains relatively small amounts of bound hydrogen.

The gaseous products can be further oxidised by the admission of additional oxygen or air to produce non-hazardous products, carbon dioxide and water. The advantage of this process compared with combustion is that it can all be carried out in a tightly controlled containment and the loss of hazardous or radioactive materials in the off-gas is therefore much reduced or even eliminated altogether. Another significant benefit is the low volume of off-gas that simplifies off-gas handling, including the possibility of achieving essentially zero gaseous releases. The process constitutes a convenient means for accomplishing the following objectives referred to in the foregoing discussion.

- The process can be used to convert graphite into a form where any Wigner energy is removed.
- The process can be used to gasify the carbon in the graphite.
- The process can be used to retain the gasified carbon in a form for further processing as necessary.
- The process can be used to separate efficiently the carbon in the graphite from other radioactive elements present in the moderator to allow ease of handling, and facilitate the discharge of the carbon mass to atmosphere.

— The process can be used to process individual blocks or particles of graphite removed from the reactor core in a conventional manner.
— However, the process can also be used to react the moderator graphite slowly, in-situ, with very dilute steam in an inert atmosphere as a means of removing the graphite moderator from the reactor core in a slow and controlled manner without the need for human intervention in the reactor core.

Radioactive secondary waste from the reaction phase, or from further processing of the carbon dioxide prior to discharge, can be dealt with in any conventional manner appropriate to normal procedures of the nuclear plant concerned.

4. EX-SITU PROCESSING OF GRAPHITE

Figure 2 provides an overview flow diagram of the process as adapted to process radioactive graphite. Radioactive graphite is remotely removed from the reactor core by means of water jet or mechanical cutters. Graphite pieces and water are introduced into a size reduction wet grinder where the graphite is reduced to <1.0 cm size. The size-reduced graphite and water are slurry fed directly into the reformer by means of a slurry injector pump, without any other pre-treatment or handling required. Alternatively, graphite can be size reduced to <4.0 cm for direct injection into the Reformer by means of a mechanical screw conveyor. Other Low-Level Radioactive Waste streams can, if desired, also be processed by the Reformer.

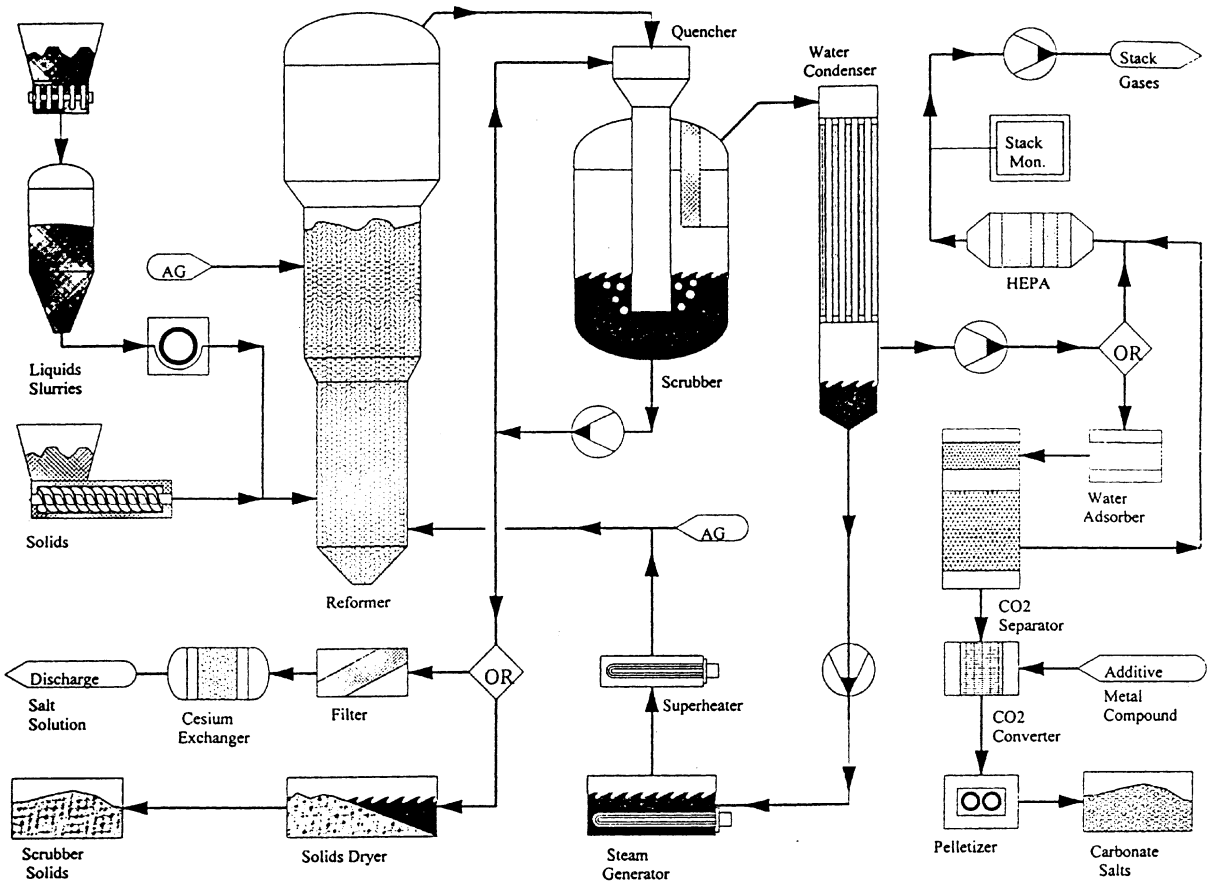

FIG 2. THOR process diagram for graphite gasification.

The Reformer fluid bed serves to evaporate all water from the graphite slurry and other liquid waste feeds and pyrolyze any organic components through destructive distillation. Energy needed to evaporate the feed water and drive the endothermic reformation is provided by operating the fluid bed in an autothermal steam reforming mode. Carbon monoxide and hydrogen produced by the in-bed steam reformation process are fully oxidised to carbon dioxide and water in the upper zone of the fluid bed by injection of oxygen. The off-gas from the Reformer contains fine particulate, including most radionuclides and all non volatile inorganic materials such as silica and calcium found in the waste, and gaseous components such as steam, carbon dioxide and gaseous radionuclides, particularly tritium, carbon-14 and iodine. The solid residue is elutriated from the Reformer by the fluidising steam and gases.

The particulates in the off-gas from the reformer are removed from the off-gas stream by a high temperature filter or wet scrubber. If only graphite is to be processed by the process, a high temperature particulate filter is all that is needed to clean all non-volatile radionuclides from the off-gas. If other streams are being processed, the wet scrubber is utilised as shown in Fig 2. Table I provides a list of typical radionuclides found in moderator graphite and how the radionuclides partition in the process.

TABLE I. TYPICAL RADIONUCLIDE PARTITION

Radionuclide	**Partitions to**	**Radionuclide**	**Partitions to**
Antimony 125	Scrubber Solution	Iodine 129	Off-Gas
Calcium 41/45	Particulate	Iron 55	Particulate
Carbon 14	Off-Gas	Manganese 54	Particulate
Cerium 144	Particulate	Nickel 59/63	Particulate
Caesium 134/137	Scrubber Solution	Plutonium 239/240/241	Particulate
Chlorine 36	Scrubber Solution	Ruthenium 106	Particulate
Cobalt 60	Particulate	Strontium 90	Scrubber Solution
Hydrogen 3	Condensate	Zinc 65	Particulate

Utilisation of the wet scrubber where necessary (Fig 2) cleans the off-gas by removing particles elutriated from the Reformer and neutralises any potential acid gases. The scrubber solution is concentrated by the hot off-gas from the Reformer to 1% to 20% by weight solids. The pH in the scrubber solution is controlled between 5.0 and 7.0 to minimise carbon dioxide absorption and to assure removal of acid gases. The salt solution can be treated by conventional means, such as direct discharge (if radioactivity levels permit), discharge after selective removal of radioactive species, or encapsulation to form solid waste. Insoluble constituents in the scrubber solution can be removed by filtration if a discharge route is chosen.

The warm, water-saturated off-gas stream can be further processed to remove essentially all the water vapour by means of a refrigerated condenser or absorption contactor/drier. The condensed water will include essentially all the tritium from the graphite. The condenser water with trace levels of tritium can be handled by one or more of the following methods. It can be recycled to provide for water cutting duty, or to supply superheated steam to the reformer. Alternatively it can be discharged as water vapour or liquid water, or used to mix with cement for solidification of other radioactive waste. Some of the iodine in the off-gas will also tend to be carried with the water.

Following the Scrubber and Water Condenser, the cool, dry off-gas consists almost exclusively of carbon dioxide and small amounts of oxygen and nitrogen. If allowed by regulation, the carbon dioxide rich off-gas can be HEPA filtered, monitored, and then discharged to the facility stack. If required by regulation the carbon dioxide can be removed from the off-gas by means of an absorber or refrigerated condenser, shown in Fig 1 as a CO_2 Separator. The concentrated carbon dioxide can be transferred to the converter for conversion to a solid carbonate salt. The remaining non-condensable gases can then be HEPA filtered, monitored and then discharged to the facility stack. The final small off-gas flow represents less than 5% of the off-gas flow from the outlet of the Reformer.

The concentrated carbon dioxide can be converted to a solid, inert carbonate compound using existing technology. The Converter consists of the process equipment needed to react the carbon dioxide with calcium or magnesium oxides or metals to produce carbonate salt, preferably insoluble. The interaction of carbon dioxide with MAGNOX fuel element debris waste is described in several publications [1].

The carbonate salt can be formed into dense pellets or powder and can conveniently be used to fill void spaces in existing radioactive waste disposal containers.

5. IN-SITU PROCESSING

In-situ processing of graphite requires that the graphite in the reactor core be subjected to conditions suitable for gasification of graphite. The in-situ reactions can be performed by one of the following methods:

(a) Recirculate carbon dioxide, nitrogen or other inert gas through the reactor using normal in-plant hardware with addition of small, controlled amounts of steam or oxygen. A side stream will need to be continuously extracted from the loop for removal of carbon monoxide and hydrogen. To mitigate potential hydrogen explosion issues it would be desirable to insert a catalytic hydrogen converter in the treatment loop to react any hydrogen to water. This option will require the injection of a small amount of oxygen into the catalytic converter.

— For the addition of trace amounts of oxygen, the reactor circuit will need to be maintained above 250^{o}C for oxidation reactions to happen in sufficient time to allow usage of less than 5 percent oxygen concentration in the recirculating gases. The use of restricted oxygen levels is recommended to eliminate any potential explosion reactions.
— For the addition of steam, the reactor circuit will need to be maintained above 350^{o}C for reformation reactions to proceed at reasonable rates.

(b) Inject and remove gases in the reactor without the use of other in-plant equipment. This method involves isolation of the reactor from the balance of plant systems. An external gas recirculation loop can be utilised to inject gases into the reactor and provide removal of gaseous reaction products. Selected areas of the reactor can be maintained at high temperature by means of injection of superheated gases at 400 to 900^{o}C or by generation of the needed heat inside the reactor. Heat generation inside the reactor can be achieved by the insertion of electrical or combustion tube heaters placed in one or more of the fuel channels. The in-situ reaction utilising this method would allow the preferential removal of the graphite in selected areas of the reactor to remove graphite in a planned sequence. This is an extremely valuable safety feature, since it allows the graphite to be removed in a structurally secure manner,

avoiding the possibility of collapse of a weakened moderator structure during the later stages of removal. The feasibility of local removal of graphite by this method is further aided by the decreased thermal conductivity of graphite in end-of-life moderators, which occurs as a result of neutron irradiation. It is estimated that over 75 percent of the graphite could be removed this way. The injected gases can consist of one or more of the following gases: carbon dioxide, steam, oxygen, and/or other reactive gases. Final removal of the last quantities of graphite could, for example, be achieved by reverting to water jet cutting for removal of graphite followed by gasification performed in the fluid bed Reformer as described above.

6. CONCLUSIONS

(1) Extensive experience exists with the technique of pyrolysis/steam reforming for the treatment of organic Low-Level Radioactive Waste.

(2) This process can be adapted for the treatment of radioactive graphite.

(3) The process can be applied to pieces or particles of graphite remotely removed mechanically or hydraulically from a reactor core.

(4) The process can also be applied to gasify graphite in-situ within the reactor core.

(5) Carbon dioxide product from the gasification can either be released to atmosphere or, if required, reacted to form a solid carbonate product which can be used to in-fill voids in other radioactive waste.

REFERENCES

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[2] HESBOL & MASON, “Method for the Volume Reduction and Processing of Nuclear Waste”, US Patent 5,909,654, June 1999.