NEWS

Nuclear waste disposal: Fuelling new science

In the journal Science and Technology Review of the Lawrence Livermore National Laboratory (LLNL) the article The Safe Disposal of Nuclear Waste (March 1996, 106) by W. L. Clarke indicates how serious US is about nuclear energy, more importantly how serious it is about the safe disposal of nuclear waste. More than 20,000 tonnes of spent fuel from nuclear power plants are at present stored temporarily at 109 reactor centres across the United States in pools of water (which act as radiation shield and as coolant) and in special concrete or steel casks. By 2010 about 71,000 tonnes of nuclear waste will have to be disposed off. All nations using nuclear power have this problem and are exploring methods of disposing safely radioactive waste.

The US government has laid extremely stringent health and safety regulations. Nuclear waste must be contained for at least 1000 years after permanent closure. Even after this period (of 1000 years) the release of any radio nucleide from the system cannot exceed one part in 100,000 of the amount of nucleide initially present and this cannot be exceeded for 100,000 years! The radioactive material remaining after 10,000 years should correspond to the unmined deposits of uranium ore of comparable size. The environment conditions laid out are unprecedented for any man-made system.

The idea is to package the waste in a two-layer containment vessel ('barrier') placed on rails in horizontal tunnels about 300 metres underground. The tunnels will remain open for 100 years to permit monitoring and to allow for

retrieval if any problem is discovered (or if some use is found for the spent fuel). After this period the tunnels will be filled and sealed.

The US Department of Environment will be responsible for building and operating the underground nuclear repository. An act of US Congress has directed DOE to concentrate on one site at Yucca Mountains, 145 miles from Las Vegas. (Newspaper reports say that immediately after the announcement of this, many citizens of the state have strongly protested against the choice of this site.)

The first task undertaken is the choice of the materials for the containers and then come various processes that may have to be used. Metal alloys, plasma sprayed carbon steels, nickel-rich stainless steel alloys, the super stainless steels with increased nickel content which give them an added corrosion resistance are all being considered. A nickel iron, chromium alloy (40-60%) nickel – called Alloy 825) developed for handling sulphuric acid is a serious candidate for the inner barrier because of its excellent corrosion resistance, oxidation resistance and its mechanical properties; nickel and titanium alloys of various compositions are also candidates and are subjects of study.

A major concern is water – because of the possible corrosion of the package. Water can dissolve and transport waste nucleides. The rates of dissolution of nuclear waste, the oxidation of uranium oxide, the failure of zirconium alloy cladding and the release of radio nucleide from the cladding material are being studied in great detail. The range of studies undertaken is astounding and will surely add much to our knowledge of chemistry, long-term corrosion, stress corrosion under varying temperatures, etc.

At the meeting of the Materials Research Society, USA, a rather novel and promising method of preventing water from reaching the containers was presented. This is to use the heat given off by the waste storage containers to produce a dry environment not only in the containers themselves, but also to keep the rock 100 metres away dry.

LLNL has long been experimenting on vitrifying nuclear waste. Glass is highly durable if kept dry and the effect of water on vitrified materials is being studied systematically. Computer models based on glass-water reactivities will allow more confident predictions. However if water does contact the vitrified waste in the repository, necessary processes are being evolved (using additives?), so that the glass can slowly transform into a composition similar to those found in the soils. Detailed experiments seem to indicate that glass can last for more than several thousand years without disintegration. Computer models based on glass-water reactions will allow more confident predictions.

The possible effects of radiation damage and the consequent possibility of crevice corrosion are also subjects of experimental and computer studies.

There is a major programme on the effect of microbial attack and how they can drastically change chemical environment. In acidic conditions microbes can cause high corrosion rates between temperatures of 30°C and 120°C. The

near-field studies include geochemistry, geohydrology, hydrothermal interaction and geomechanics.

This is a gargantuan undertaking in which almost every conceivable aspect of materials science is being studied.

Apart from possible solutions for the disposal of nuclear wastes, this programme may contribute greatly to newer aspects of material science. Some of the results have already been published. The rest will not only be discussed in con-

ferences but are also expected to appear in open literature.

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Bacteria precipitate arsenic

Mining sites are important sources of pollution. The oxidation of metallic sulphides, under the action of surface waters, produces sulphuric acid and the metals released are soluble in these acidic waters. A number of metals and metalloids, including arsenic, are poisonous and pose a threat to the environment.

Primitive forms of life can colonise these extreme conditions. Chemolithotrophic bacteria draw their metabolic energy from electrons released during oxido-reduction. Bacteria such as Thiobacillus ferrooxidans catalyse oxidation reactions of iron sulphide and are used industrially to retrieve metals in poor ores (bacterial leaching). Arsenic contained in sulphides can be released; according to its state of valency, it will be soluble (As³⁺) or insoluble (As⁵⁺). That is, it will either be a poison released in the medium or it will precipitate in a relatively stable form with ferric iron.

The mining site of Carnoulés, in Gard, in the South of France, abandoned for the past 30 years, includes quarries where lead sulphide ore was exploited. A sizeable stock of wastes resulting from the processing of ore, containing another 10% of iron sulphide, lead and arsenic were also found. Water from the Carnoulés stream is very acidic (pH 2.5-3.5) and rich in metals (Fe, Zn, Pb) and causes pollution over several kilometres downstream. This was already

Source: Technical News, May 1996, Centre for Documentation on Universities, Science and Technology, Embassy of France, New Delhi.

studied by Michard and Faucherre in 1970. Scientists noted high concentrations of arsenic (100 to 200 mg/l – about 2000 times greater than the limit approved for drinking water) in the upper portion of the stream. At 1.5 km downstream, acidic waters do not contain more than 0.2 to 4 mg/l of arsenic as this element gets deposited on the way. In fact, the sediments of this stream are essentially composed of iron and arsenic; in the upper part of the stream, there is about 9 to 20% of arsenic in the form of yellow deposits of ferric arsenate. These sediments show structures of bacterial construction which remind us of the most ancient forms of life that appeared on earth:stromatolites.

Research was then directed to the study of these deposits. Forms that could be identified with their morphology and their size such as bacteria were observed under a sweeping electronic microscope. Scientists discovered that bacterial stromatolites could thrive in continental acidic waters. In just a few days, the bacterial colonies formed extending bacterial carpets on sulphide sand deposits. Semi-quantitative analyses with the electron microscope could show that the bacteria had a covering of arsenic and iron.

In the second stage, bacterial species present in the acidic waters have been determined in the laboratory through culture on selective mediums. The most abundant forms are of the *Thiobacillus* type (*Th. acidophilus, Th. ferrooxidans*) and the *Leptothrix* type. The role of bacteria on the precipitation of iron

arsenates was studied in the laboratory by measuring the quantity of arsenic precipitated by different strains of bacteria. The sample taken was the arsenic present in soluble form in the acidic water of Carnoulés. These results were compared with the precipitates in the absence of these bacteria. This experiment, followed for several weeks, showed that two bacterial strains enable the precipitation of 80% of the arsenic, whereas without bacteria, only 25% of the arsenic precipitated. The bacteria thus favour oxidation of arsenic and the precipitation of arsenate. Lead, which is also present in strong concentrations (1.1 to 2 mg/l) in the acidic waters of Carnoulés, precipitated with the arsenic (0.25% Pb in bacterial sediments). Now, it has to be determined if bacteria catalyse only chemical precipitation reactions (oxidation As³⁺-As⁵⁺), by lifting an electron on the way or if they use arsenic in their metabolism.

As for environment, the bacterial action is positive. There is on-the-spot storing of most of the arsenic (and lead); but, these deposits are fragile and can be quickly eroded and carried downstream by a heavy rain. This remarkable site with its chemical 'reactor' and acidic ecosystem forms a natural laboratory to study and quantify the flow of arsenic and metals as well as specify the role of bacteria.

The biological control of toxic arsenic levels in water assumes importance in view of the recent arsenic poisoning tragedy in West Bengal (Curr. Sci., 1996, 70, 976-986).