Accelerated carbonation study for the prediction of long term performance of the Nirex Reference Vault Backfill in radioactive waste disposal

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ABSTRACT

The use of cement based materials could be widespread in the long term management of radioactive materials in the United Kingdom. One such material could be the Nirex Reference Vault Backfill (NRVB) which is specially designed by United Kingdom Nirex Limited (Nirex) to act as both a physical and chemical barrier within a deep geological repository. The NRVB can absorb radioactive carbon dioxide ($^{14}CO_2$) generated from certain organic wastes in the repository. To prevent the release of $^{14}CO_2$ from the repository, two factors should be satisfied. One factor is that there is sufficient NRVB in the vault. The other factor is that the gas generated has enough time to react with the backfill.

The objectives of this work are to determine the carbon dioxide absorption capacity of the NRVB and develop a kinetic model which can be used for the prediction of the carbonation rate, i.e. the rate that the lime component in the NRVB material reacts with carbon dioxide and water to form solid carbonates. One-dimensional accelerated carbonation experiments on 25mm NRVB cubes have been carried out under selected reaction conditions to simulate the underground environment. At present, the effects of temperature, pressure and saturation degree on the carbonation of the NRVB are being investigated. Reaction rate curves and the effects of these conditions will be presented.

INTRODUCTION

Material that has no further use and is above a certain level of material radioactivity is known as radioactive waste. As a hazardous waste, radioactive waste can harm people and the environment and therefore is carefully controlled. In the UK, the source of most radioactive waste is the nuclear power industry, which includes manufacture of nuclear fuel, nuclear power stations, reprocessing of spent nuclear fuel and research & development programmes. Outside the nuclear power industry, defence activities, medical and industrial sources also contribute to the radioactive waste in the UK.

According to the level of radioactivity and the heat produced by this radioactivity, these radioactive wastes are divided into three main categories: Low Level Waste (LLW), Intermediate Level Waste (ILW) and High Level Waste (HLW), which are described in table 1. It has been reported that in the UK the total volume of radioactive waste that exists today and is forecast in the future is 2.3 million cubic metres, 99.9% of which are LLW and ILW [1].

LLW	Wastes other than those suitable for disposal with ordinary domestic refuse but not exceeding specified levels of radioactivity. Overall, the major components of LLW are soil, building rubble and steel items such as ducting, piping and reinforcement from the dismantling and demolition of nuclear reactors and other nuclear facilities, and the clean up of nuclear sites. However, at the present time most LLW is from the operation of nuclear facilities and this is mainly paper, plastics and scrap metal items.
ILW	Wastes exceeding the upper boundaries for LLW that do not generate sufficient heat for this to be taken into account in the design of waste storage or disposal facilities. The major components of ILW are metal items such as nuclear fuel casing and nuclear reactor components, graphite from reactor cores, and sludges from the treatment of radioactive liquid effluents
HLW	Wastes in which the temperature may rise significantly as a result of their radioactivity, so this factor has to be taken into account in the design of waste storage or disposal facilities. Initially HLW comprises nitric acid solutions containing the waste products of reprocessing spent nuclear fuels.

Table 1 Categories of radioactive waste in the UK [1]

In support of government policy, United Kingdom Nirex Ltd (Nirex) develops and advises on safe, environmentally sound and publicly acceptable options for the long-term management of radioactive materials. To provide long-term management for LLW and ILW, Nirex has developed a Phased Geological Repository Concept (PGRC). This concept is based on a deep geological repository and includes a number of stages in the management and eventual disposal of radioactive waste:

- **Packaging the waste** The wastes would be encapsulated within cement-based grouting material within stainless steel or concrete containers by waste producers;
- **Surface storage**. Packaged wastes would then be held in surface stores around UK;
- **Transport**. The waste packages would be transported to a repository;
- **Waste emplacement** Waste packages would be emplaced in large purpose-built vaults which are excavated in a stable geological environment deep under ground. This would provide a significant barrier of several hundred meters of rock;
- **Operational phase** The waste would be stored underground for an extended period, during which the repository and its contents would be monitored;
- **Vault Backfilling** When and if there is sufficient confidence in the system, the repository vaults could be backfilled with a specially developed cement-based material;
- **Post-closure phase** When backfilling has been completed, the repository can be closed and sealed. The multiple barriers would provide long-term containment of radioactivity in the repository without further human management.

The specially developed cement-based backfill material in PGRC is Nirex Reference Vault Backfill (NRVB). The NRVB is designed to chemically conditionally condition the in-flowing underground water to high pH and have a high porosity, which allows gas to disperse in the vault volume. The NRVB would also absorb the radioactive carbon dioxide ($^{14}CO_2$) which is generated from the degradation of particular radioactive materials [2]. To prevent the release of $^{14}CO_2$ from the repository, two factors must be satisfied: that there are enough alkaline components in the NRVB to absorb all the $^{14}CO_2$ generated and that the reaction rate is fast enough to ensure that the $^{14}CO_2$ cannot escape the repository.

$$Ca(OH)_2 + CO_2 \rightarrow Ca(CO)_3 + H_2O \tag{1}$$
$$C_xS_yH_z + xCO_2 \rightarrow xCaCO_3 + ySiO_2 + zH_2O \tag{2}$$
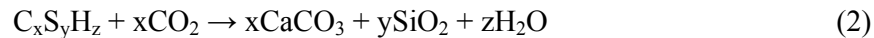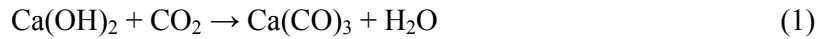
The carbonation of the NRVB can be described by Equation 1 and Equation 2. Although the carbonation of NRVB is a gas-solid reaction, the actual reaction takes place in the aqueous phase, with dissolved carbon dioxide reacting with calcium ions in pore solution to form calcium carbonate precipitates. Continuing carbonation requires the diffusion of carbon dioxide through the reacted layer to uncarbonated material, a process that may take place in either the gaseous or aqueous phases. As a result, the rate and extent of carbonation largely depends on the conditions under which the reaction is taken place [3], such as the atmosphere pressure, the concentration of carbon dioxide, the reaction temperature, the relative humidity, as well as the degree of water saturation of the pore structure.

Since the repository would be deep underground, the pressure inside could be very high (6 to 7 MPa). Moreover, during the backfilling, heat would be generated due to the hardening of the NRVB and the temperature in the repository could reach up to 80ºC. Although a great amount of research has been done on the carbonation of cementitious materials under moderate conditions, the data cannot be applied to the conditions in the repository. Nirex has already conducted some researches on the carbonation of the NRVB, focusing on the effects of the water saturation degree of the pore structure [2, 4]. However, more work is required to achieve a better understanding of the process.

To predict the NRVB performance in the repository deep underground, single dimensional accelerated carbonation tests have been done on the NRVB samples to explore the effects of temperature, concentration of carbon dioxide and water saturation degree of the pore structure.

EXPERIMENTAL PROCEDURES

Specimen Preparation

The NRVB is a high porosity cementitious material based on a mixture of ordinary Portland cement (OPC), hydrated lime (calcium hydroxide) and lime stone flour ($CaCO_3$). The specimens of NRVB used in this study were 25mm cubes, prepared by Nexia Solutions Limited. Each individual cube was wrapped in a tissue that had been soaked in saturated lime solution to prevent pre-carbonation during delivery and storage.

As the NRVB specimens received were damp, the degree of water saturation, also known as water content, in the specimens have to be controlled by conditioning them under certain relative humidities (RH). In this research, the specimens of NRVB were divided in three groups, and stored in two desiccators, in which 75% RH and 100% RH were maintained by saturated NaCl solution and deionised water respectively. The masses of the specimen were monitored continually and conditioning continued until a constant mass was reached. To prevent the carbonation with CO_2 in the air, nitrogen was flashed into the desiccators every time they were opened.

To simplify the interpretation of the experimental results, the conditioned specimens were sealed by casting into epoxy resin and left only one surface exposed. As a result of doing this, the carbonation reaction proceeded in a single dimension which allowed the determination of carbonation rate easier than that of three dimension reaction. Due to the lack of environmental control facility, the operations of the specimens casting were performed in air. However, the sealed specimens were placed back into desiccators to allow the resin to cure.

Equipment and Method

The carbonation rig used in this study is shown in Figure 1. The static reactor was a 5 litre stainless steel chamber (1) wrapped with heat insulation. To control the temperature in the reactor throughout the reaction, a thermostat (2) was connected to the heat exchanging plate inside the reactor. For each experiment, one sample was placed on the heat exchanging plate, under which a glass basin filled with water or saturated NaCl solution was placed to maintain the relative humidity inside the reactor. The reactor was then sealed with clamp. Prior to initial pressurisation, the vacuum pump connected to the reactor outlet (3) was used to evacuate the residual air in the reactor, and then pure CO_2 was inlet into the reactor. Once a selected starting pressure is reached, the inlet valve (4) was shut down, and a stopwatch (5) was switched on immediately. The pressure drop in the reactor was monitored constantly by a digital pressure gauge (6) throughout of the reaction process. The temperature and relative humidity within the reactor were also detected by a Vaisala HMT334 temperature/humidity transmitter (7).
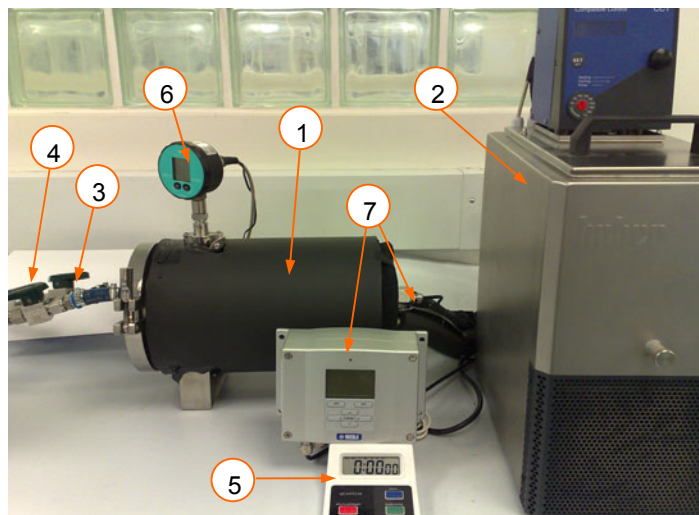

Figure 1 Carbonation rig

Table 2 shows the reaction conditions selected for the accelerated carbonation experiments. This experimental design allowed us to study of the effects of water saturation degree in the sample, the carbon dioxide pressure as well as carbonation temperature.

Group 1	P=3bar, T = 20°C	Saturation degree = 75%RH, 100%RH
Group 2	Saturation degree = 75%RH, T = 20°C	P=1.5bar, 3bar, 4bar
Group 3	P=3bar, Saturation degree = 75% RH	T = 20°C, 35°C, 50°C

Table 2 Reaction conditions for accelerated carbonation experiments

RESULTS AND DISCUSSION

During carbonation, the conversion of the NRVB sample is defined as Equation (3):

$$X = \frac{(P_0 - P_t) \times V}{RT \times N_0} \tag{3}$$

Where X is the conversion of the NRVB sample, P_0 is the initial pressure in the reactor when the reaction starts, P_t is the pressure at time t, V is the volume of the reactor, R is the gas constant, T is the reaction temperature, and N_0 is the initial quantity of reactive calcium in the specimen. Adopting the model provided by Harris [5], the carbonation capacity of NRVB is considered to be the reactive calcium content of the material.

A common feature of the carbonation progress of hydrated cementitious materials is the assertion that a square root relationship exists in the form [6]:

$$X = k\sqrt{t} \tag{4}$$

Where t is the exposure time and k is a coefficient dependent on material parameters. Equation (4) is based on the assumption that for any environment the diffusion coefficient is constant across the depth of the carbonated layer and that the quantity of calcium hydroxide in the volume element under consideration is constant. To compare the experimental data with Equation (4), the reaction rate curves are usually plotted in the form of X vs. $t^{0.5}$.

The Effect of Temperature

From Figure 2, we can see, during the first 600 minutes, 35ºC and 50ºC show slightly higher reaction rates than that at 20ºC. After that, the reaction rate at 50ºC dropped faster than those at the other two temperatures, and as a result the final conversion of the specimen at 50ºC was the lowest. The highest conversion was achieved under the reaction temperature of 35ºC.
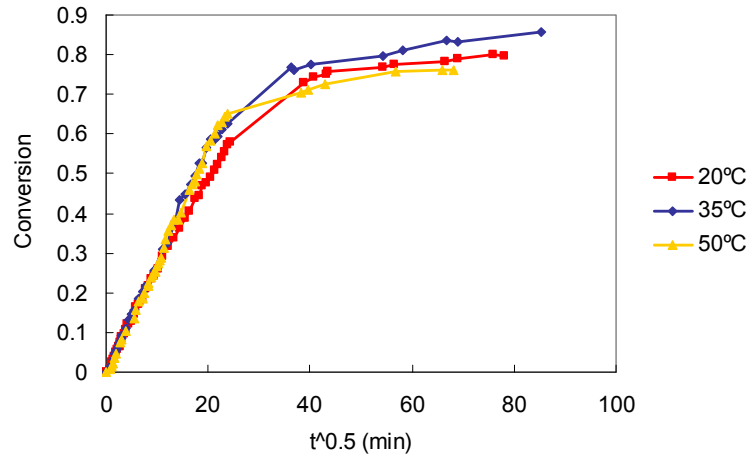
Figure 2 The effect of temperature (P = 3bar, RH = 75%)

Apparently the effect of temperature variation within the range 20ºC-50ºC on the rate of carbonation is rather small. This observation agrees well with Loo et al. [7], who concluded from their investigation that at around 65% RH the rate of carbonation is very weakly sensitive to temperature.

The Effect of Pressure

It is known that, in the carbonation of concrete, increasing the CO_2 concentration or CO_2 partial pressure can increase the reaction rate, as high CO_2 concentrations would accelerate the gas diffusion into the pores of the concrete. However, Figure 3 shows that CO_2 pressures ranging from 1.5 bar to 4 bar do not affect the rate of carbonation of NRVB specimens significantly. This may be due to the pressures used in the present investigation (1.5bar, 3bar and 4bar) being rather close in magnitude. Loo et al. [7] also observed that, for concrete with strength higher than 40 MPa, low magnitude of variation in CO_2 concentration did not affect the rate of carbonation.
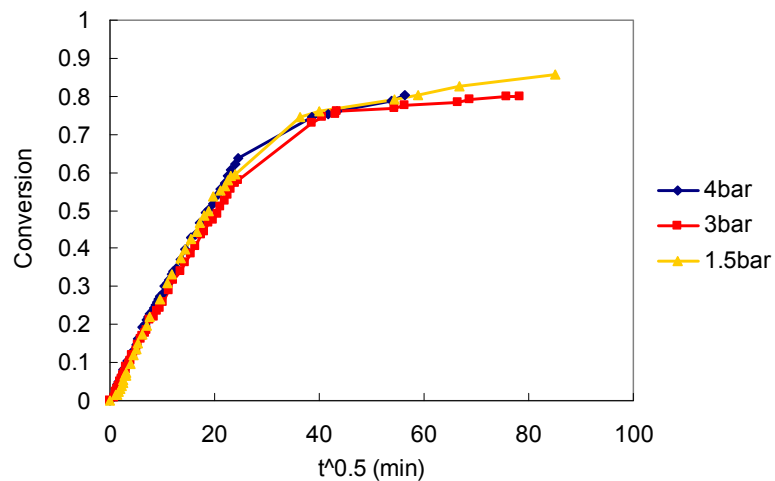

Figure 3 The effect of pressure (T = 20ºC, RH = 75%)

In the repository which is deep underground, the gas pressure can be around 7 to 8 bar. However, the concentration of CO_2 within the repository is still unclear. Therefore, in order to cover all possibilities, more experiments have to be carried out with a wider range of CO_2 concentrations

The Effect of Degree of Water Saturation

After conditioning in 100% RH, the water content left in NRVB was approximately 583 kg m^{-3}, and the pores were 100% saturated. However, samples conditioned in 75% RH only had a water content around 209.7 kg m^3, and the degree of water saturation in the pores was only 36%.

The reaction rate curves in Figure 4 demonstrate the importance of water content. For the sample conditioned at 75% RH, the reaction rate was very fast initially, but as the reaction proceeds, the reaction rate slows down, gradually approaching zero. A conversion of 80% was achieved within 102 hours. In contrast, the reaction rate of the saturated sample was slow but almost constant throughout the reaction, and the conversion at 102 hours was only 24%.
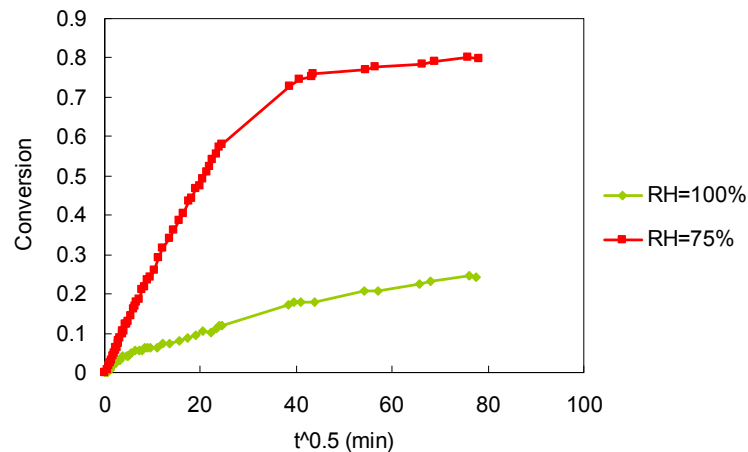

Figure 4 The effect of degree of water saturation (P = 3bar, T=20ºC)

In the real situation, after the NRVB is filled in to the repository, it is assumed the relative humidity inside the repository would be around 75%. As the underground water flows into the repository, the relative humidity would increase gradually, finally reaching to 100%, which means all the pores of NRVB would be filled with water. According to the experimental results, it can be predicted that the CO_2 uptake by NRVB would be more and more difficult as time goes by.

Preliminary Kinetic Study

The reaction rate curves shown in Figures 2 to 4, except the reaction curve at 100% RH, show at least two distinct linear segments for each sample, indicating that at least two stages of diffusion-controlled reactions exist.

The value of k depends on three factors as shown in Equation (3):

$$k = \frac{2Dc}{\alpha} \qquad (5)$$

Where c is the concentration of carbon dioxide, α is the amount of reactive calcium contained in a unit volume of fresh specimen and D is the diffusion coefficient of carbon dioxide. In this work, α is constant during the reaction, but c kept decreasing as the reaction took place in batch reactor. D is a factor restricted to the permeability of the pore structure. During the reaction, calcium carbonates are formed and precipitated in the pores. Meanwhile, water is produced during the reaction and with increasing pore water content, the pore network becomes blocked. The loss of free gas path results in a decrease in D. Theoretically speaking, by the time all the pores are blocked, the reaction virtually stops before 100% conversion is fulfilled.

CONCLUSIONS

Of the parameters tested, the rate of carbonation of NRVB is influenced mainly by the degree of water saturation of the pore structure. In comparison, the effect of CO_2 pressure and temperature is insignificant. The reaction under unsaturated conditions occurs in two/three stages:

i) an initial rapid stage,

ii) a slower intermediate stage (this stage is not for sure due to the lack of experimental data), and

iii) a very slow final stage when carbonation virtually stops.

These stages are controlled by the openness of the pores in the NRVB.

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