THE CARBONATE DISSOLUTION PROCESS FOR THE MANAGEMENT OF MAGNOX FUEL ELEMENT DEBRIS - SMALL SCALE STUDIES OF THE SPRAY DISSOLUTION OPTION

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ABSTRACT

Dissolution in carbonic acid has been suggested as a possible conditioning option for Magnox fuel element debris accumulated within storage vaults at UK nuclear power stations. One approach would be to spray water saturated with CO_2 onto the piles of debris. This paper reports work carried out to demonstrate the chemical viability of spray dissolution. Small rigs have been used to investigate the important parameters affecting carbonate dissolution. The response of a continuous flow spray dissolution to changes in process variables such as gas and liquid flowrates, temperature, liquor recirculation and Magnox inventory has been determined. Reaction rates of 1 - 2 $g/dm^2/day$ can be obtained. The residues from the dissolution of non radioactive Magnox samples have been characterised. The process is shown to be inherently self-limiting and experiments that simulated a range of possible faults, such as interruption of water or CO_2 supplies and temperature excursions are described.

INTRODUCTION

The fuel in Britain's first generation nuclear power reactors consists of natural uranium metal contained in a Magnox can. The clad material is typically > 99% magnesium alloyed with other metals such as aluminium or zirconium. The alloy's name, Magnox, is used to describe this general reactor type. The typically 1 m long cans are stacked up to form fuel assemblies in channels within the reactor core. After irradiation approximately 0.5 kg of extraneous can material is stripped from each element and stored in shielded vaults at the power station site. The current arisings of this waste amount to about 5000 kg/year at each station. The bulk of this material is only slightly radioactive and is classified intermediate level because of activated constituents in the Magnox and the presence of irradiated Nimonic components containing Co-60, with a specific activity of 1.5×10^{10} Bq/gramme after 5 years decay.

Various options for the conditioning of this waste have been discussed by Bennett et al [1]. In addition to the more conventional encapsulation and packaging disposal routes, the dissolution of the magnesium component of the waste by carbonic acid was shown to be a potentially very useful method of volume reduction. The high chemical reactivity of the Magnox is exploited to provide selective attack of the fuel element debris by a weak reagent - in this case carbonic acid. Both small scale and pilot plant trials have shown that the bulk of the radioactivity in the waste remains undissolved. These trials and the underlying radiochemical aspects of the process have been described by Bradbury [2].

Two conceptual methods of exploiting the chemistry of Magnox dissolution have been identified. The first is termed submerged dissolution and involves immersing the waste in a vessel supplied with carbonic acid. This is a batch process suitable for conditioning retrieved material. The second approach is termed spray dissolution. In this application the carbonic acid reagent is applied as a spray to the top of a heap of fuel elements debris. After percolating down through the heap, the magnesium rich liquor is recovered at the base for filtration and any ion exchange operations that may be required before eventual discharge. This method has been considered for the in-situ treatment of fuel element debris within the station vaults.

This paper examines some of the chemical and chemical engineering aspects of the spray dissolution process, with a view to establishing the basic chemical viability of this novel method of conditioning radioactive wastes.

DISSOLUTION CHEMISTRY

The chemistry of carbonate dissolution has been discussed by Bradbury [2]. The important magnesium species are Mg^{2+}, $MgHCO_3^+$, $MgCO_3$ and, to a lesser extent, $MgOH^+$. The speciation and solubility of magnesium in carbonated water is strongly pH dependent (Fig. 1.). The peak solubility is in excess of 4500 weight parts per million (ppm) at 25 C and is obtained at a pH of 7.2. Laboratory studies [2] show good agreement between solubilities measured in the laboratory and those calculated from the appropriate dissociation constants for the reactions involved. Note that the maximum solubility decreases with temperature, being about 1000 ppm at 70 C and less than 100 ppm at 95 C. This decrease is primarily due to the fall in CO_2 solubility with temperature.

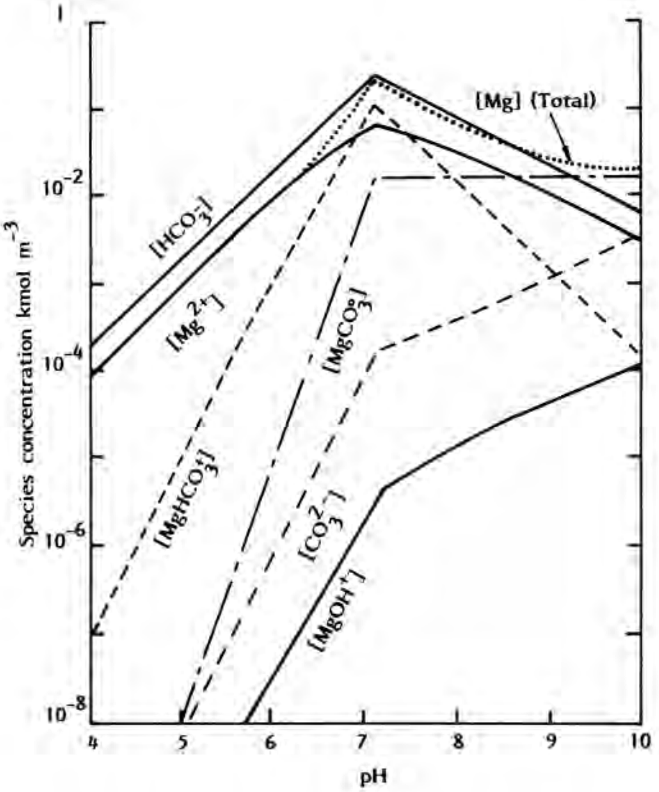

Fig. 1. Species Concentrations as a Function of pH at 25 C.

The overall stoichiometry of the reaction can be represented as:

$$Mg + 2\ H_2CO_3 = Mg(HCO_3)_2 + H_2$$

At pH values greater than 7 the bicarbonate is converted to carbonate and the limiting factor is the solubility product of magnesium carbonate, $MgCO_3$, ($[Mg^{2+}]\ [CO_3^{2-}] = 10^{-5}$ at 25 C). At pH values below 7 the solubility is limited by the availability of anions to balance the charge on the Mg^{2+} ions.

Vault stored Magnox is susceptible to corrosion by water, either present as liquid within the vault or from moisture in the ambient air in

$$Mg + 2\ H_2O = Mg(OH)_2 + H_2$$

This corrosion product can be reacted in a carbonate system in

$$Mg(OH)_2 + 2\ CO_2 = Mg(HCO_3)_2$$

Thus, hydroxide surface films on aged Magnox do not prevent the dissolution process. Note that hydroxide film corrosion does not produce hydrogen as a byproduct, unlike the reaction with magnesium metal.

Reaction rates for submerged dissolutions have been reported by Bradbury [2]. The rate is affected by the usual parameters - temperature, dissolved CO_2 concentration, pH and dissolved magnesium concentration. Because ion exchange may be required for the effluent from the process, it is desirable to operate at relatively high magnesium loadings in order to reduce the volumes of liquor to be treated. A target outlet magnesium concentration of 2000 ppm has been adopted within CEGB as a reasonable compromise that gives an adequate safety margin for the avoidance of problems that could arise due to $MgCO_3$ precipitation from highly concentrated solutions. At this concentration typical corrosion rates are around 1 - 2 g/dm^2/day which corresponds to a surface metal loss of about 0.1 mm/day. Although this rate is low in comparison with that obtained, for example, by dissolution in strong acids it is nevertheless sufficient to enable the convenient processing of the contents of a typical debris vault over a period of about 1000 days.

EXPERIMENTAL OBJECTIVES

In order to establish the chemical characteristics of the spray dissolution option it is necessary to acquire information about several features of the process. The experiments reported in this paper were designed to provide that information. The process features selected for investigation were as follows:

1. dependence of the reaction rate upon a number of process parameters including temperature and inlet dissolved magnesium concentration;
2. management of the hydrogen gas byproduct in a safe and efficient manner;
3. carbonation of the incoming process water;
4. composition and nature of process residues;
5. process response to potential fault conditions, in particular, the interruption of one or more essential supplies.

The initial experiment was designed on the conservative assumption that the reaction rate would be around 2 g/dm^2/day. Calculations of hydrogen production rate and the diluent CO_2 flow needed to keep its concentration below the explosion limit in air (4% by volume) enabled the determination of the maximum reactive surface area that could conveniently be accommodated in a laboratory scale experiment. This resulted in the selection of a 0.5 kg Magnox heap for the first series of experiments. The results of the first test series (see below) showed that, as expected, the reaction rates achieved were, in general, less than 2 g/dm^2/day and that flow channelling effects within the Magnox heap were exerting a considerable influence upon the performance of the process. Thus, the second series of tests were conducted with a larger, 1 m deep, bed with a Magnox inventory of 10 kg. The experimental aspects of the work are described in the next section.

EXPERIMENTAL DETAILS

The experiments reported here model the behaviour of a spray of carbonic acid falling upon a heap of Magnox fuel element debris. The two reaction vessels used in the study were constructed of Perspex. The smaller (0.5 kg Magnox) was cylindrical, 0.1 m in diameter and 0.3 m deep. The larger (10 kg Magnox) has a square cross section of 0.2 x 0.2 m and was 1 m deep. A flow diagram of the experimental arrangements is given in Fig. 2.

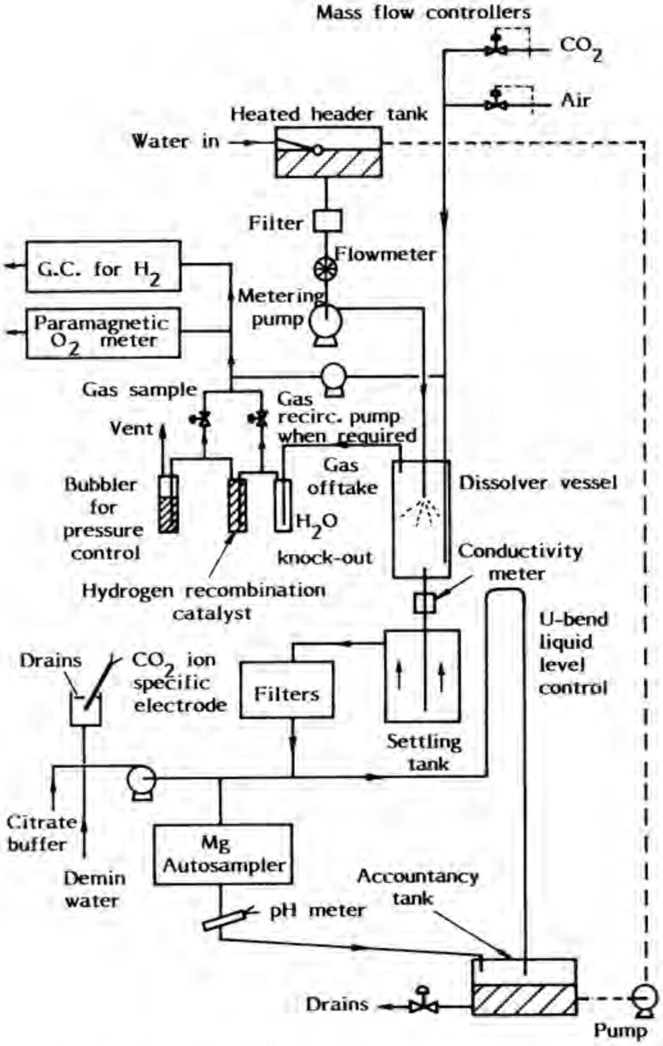

Fig. 2. Flow Diagram for the Magnox Dissolver.

Town mains water is drawn from a thermostatted top tank and pumped at up to 5 l/min through a flowmeter to the reaction vessel. Carbonation of the incoming water is achieved by spraying it into a CO_2/air atmosphere maintained within the vessel, the gas flows being provided via mass flow controllers. This simple approach results in dissolved CO_2 concentrations (measured using Ion Specific Electrodes) that are very close to those predicted from Henry's law. The liquid percolates down through the heap of Magnox fuel element debris (see Fig. 3. for a sketch of the reaction vessel), flows over a weir in the base of the vessel and passes under gravity to the downstream components of the experiment. These comprise a 25 l settler/clarifier followed by an in-line filter and a lower holding tank from which liquid can be recirculated to the top tank or discarded to the drains. CO_2 padding is provided to both tanks during recirculation runs in order to prevent the

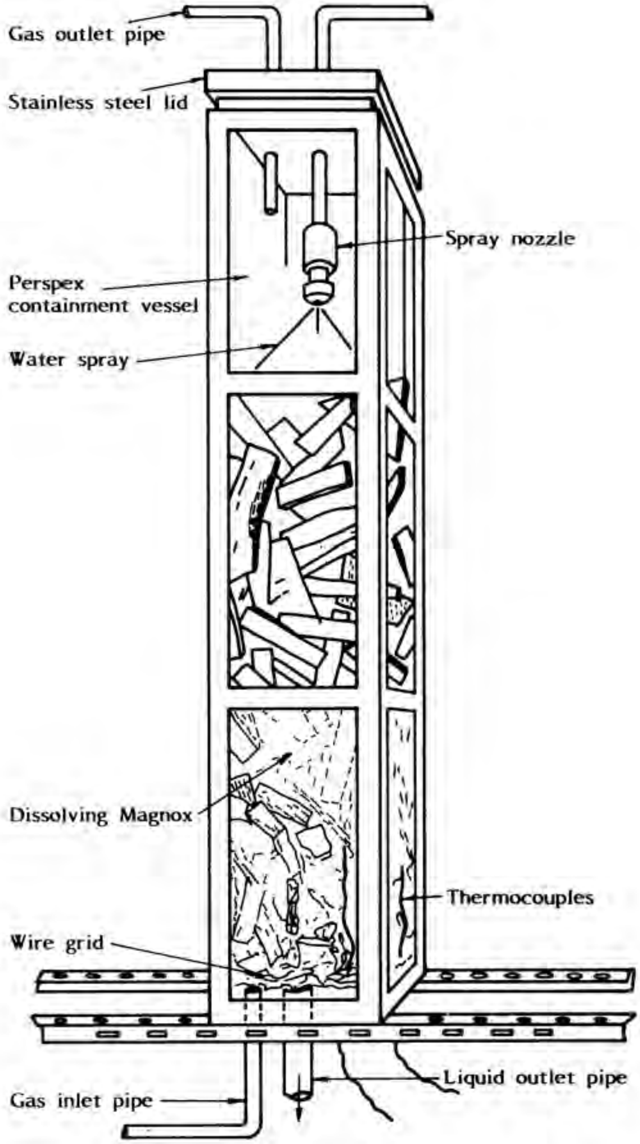

Fig. 3. 10 kg Scale Magnox Dissolver Loaded with Zr-55 Splitters.

precipitation of $MgCO_3$ from solutions having high magnesium loadings. The majority of the liquid analysis instrumentation is located in this downstream portion of the facility. Sensors for the determination of pH, conductivity and liquor CO_2 loading are provided as is an offtake to an autosampler for off-line analysis of Mg concentration.

The gas flows to the dissolver vessel are always sufficient to ensure dilution of the hydrogen produced by the reaction to a safe level. The off gas system also incorporates a platinum catalyst recombiner operated at 120 - 150 C and provision to recirculate the CO_2. Gas chromatography is used to determine the hydrogen content of the off gases. The oxygen concentration is measured using a paramagnetic analyser.

All of the rig instrumentation is interfaced to a microcomputer based data logging system. The computer monitors conditions within the experiment and is provided with the means to shut it down if a potentially dangerous situation, such as an excessive hydrogen concentration, is detected.

SINGLE PASS DISSOLUTIONS

The initial experiments examined the simplest option available on the apparatus - a single pass, straight through reaction of carbonic acid with a heap of non-radioactive fuel element debris. Typical plots of outlet magnesium concentration as a function of time for the two vessels are given in Fig. 4. (The experimental conditions used are summarised in Table I) In both cases the shapes of the plot are similar - for a period of about 400 hours the process operates in a plateau region of fairly constant magnesium concentration. Towards the end of the dissolution, the surface area available for reaction decreases and the corrosion rate and outlet magnesium concentration starts to decline.

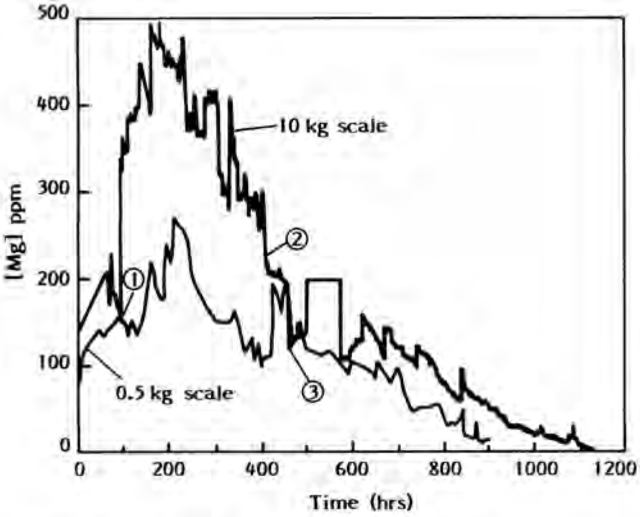

Fig. 4. Magnesium Concentrations During Once Through Dissolutions.

During the first 100 hours of operation with the larger vessel it was filled to a depth of 0.3 m in order to demonstrate that similar results to those obtained from the small vessel could be achieved. As Fig. 4. shows in both cases the outlet [Mg] was 150 - 250 ppm. The specific reaction rate under these conditions was 0.5 - 0.8 $g/dm^2/day$. After 100 hours the large vessel was completely filled with Magnox (labelled (1) in Fig. 4.), which resulted in an immediate concentration increase to over 300 ppm and a slower rise towards 500 ppm about 100 hours after the addition. The peak reaction rate during this run was 1.1 $g/dm^2/day$ which occurred 200 hours into the run. This may be compared with the maximum rate obtained on the smaller vessel, which was 1.3 $g/dm^2/day$ after 250 hours of operation.

The fluctuations in [Mg] and the corresponding rate are due to changes in the heap geometry as reaction proceeds. Channelling of the flow within the vessels leads to enhanced corrosion at certain points. Eventually, a local collapse of the heap occurs and the flow pattern changes. An interesting physical change also occurred to the splitters in the area of increased local rate - they developed a shiny surface, in contrast to the usual dull grey colouration of Magnox alloys. This was presumably due to the dissolution of the surface oxide film usually present on Magnox that has been exposed to moisture.

TABLE I

Experimental Parameters for Once Through Dissolution Experiments

	0.5 kg scale	10 kg scale
Initial mass of Magnox (kg)	0.55	9.3
Bed depth (m)	0.3	1.0
Bed cross sectional area (m^2)	0.008	0.04
Water flowrate (l/min)	0.25	0.4 - 2.2
CO_2 flowrate (l/min)	2.0	8.0
Vessel temperature (C)	25	25

During both runs the process behaved as expected from consideration of the underlying chemistry involved. Good mass balances were obtained between outlet magnesium concentration and hydrogen in the off gas. The excellent carbonation of the incoming water afforded by the sprayer system resulted in equilibration of the liquid phase chemistry at pH 6.1 - 6.3 on the low pH side of the Mg solubility curve (Fig. 1). As expected, reaction rate was directly proportional to the CO_2 partial pressure of the dissolver atmosphere. Typical analyses of the residues from the dissolutions are given in Table 2. The alloy used in these experiments is known as Zr-55, and contains 0.55% of zirconium. As the Table shows, the bulk of the residue was $CaCO_3$ from the hardness of the mains water used, together with a small amount of zirconium and traces of other elements which were probably derived from the incoming water or the pipework of the apparatus. No problems with handling the residual material were experienced, although residue handling was not an objective in these experiments. The liquor clarification and filtration were provided in order to protect the pump and sprayer during recirculation runs and no attempt to optimise this was made since the as-installed equipment proved adequate for this duty.

TABLE II

Typical Cation Analyses of Once Through Zr-55 Dissolution Residues (wt % elemental)

Al	Ca	Fe	Mg	P	Si	Zr
2.3	39.8	5.0	12.4	3.5	6.4	1.2

REACTION RATE TEMPERATURE DEPENDENCE

An important feature of the carbonate dissolution process is that it is inherently self-limiting. This is because the reaction is first order in the dissolved CO_2 concentration and the magnesium solubility decreases with increasing temperature. However, the general behaviour of a liquid phase reaction follows the Arhennius law and increases with temperature. There are thus two processes to be considered. The temperature dependence of CO_2 solubility is readily available, but that of the underlying chemical reaction rate is not. Accordingly, a series of experiments were conducted on the small dissolver in order to obtain an estimate of the activation energy for the carbonate process. Only a narrow temperature range (10 - 40 C) could be studied due to limitations imposed by the materials used to construct the apparatus. 300 g portions of magnox were loaded into the reaction vessel and corroded for 24 hours at constant temperature. At the end of this period the material was removed and replaced with a fresh tranche and the process repeated at a new temperature. After correction for the differing solubilities of CO_2, the derived rate constants (units : $g/dm^2/day/bar(CO_2)$) were shown to have an Arrhenius temperature dependence with an activation energy of 24 kJ/mole. This is low in comparison with the value of 75 - 125 kJ/mole that is more typical of liquid phase reactions. In practical terms a once through spray dissolution exhibits a slight increase in overall reaction rate at temperatures below about 40 C. At temperatures above 40 C, the rate declines sharply as the decrease in CO_2 solubility (and thus reactant availability) dominates the underlying reaction rate. This is satisfactory behaviour since it prevents runaway reaction which would be accompanied by excessive hydrogen production. An example of the temperature response of the process is given in the next section.

DISSOLUTION WITH RECIRCULATION OF LIQUOR

The single pass experiments demonstrated that greater magnesium pickup occurred in deeper beds. Fuel elements debris storage vaults at nuclear sites are typically 5 - 10 m deep. Rather than construct a vessel of this depth, which would have been impracticable on a laboratory scale, the effects of deeper beds were simulated by recirculating liquor from the bottom tank to the vessel inlet. This enabled some features of the process behaviour in deep beds to be conveniently investigated. The large vessel was used for these experiments, fully loaded with 9.8 kg of Magnox. The total liquid inventory of the system was 50 litres and by using a liquid flowrate of 2 l/min an extra 2 m bed depth could be simulated in about an hour of operation. Some typical experimental results are plotted in composite Fig. 5.

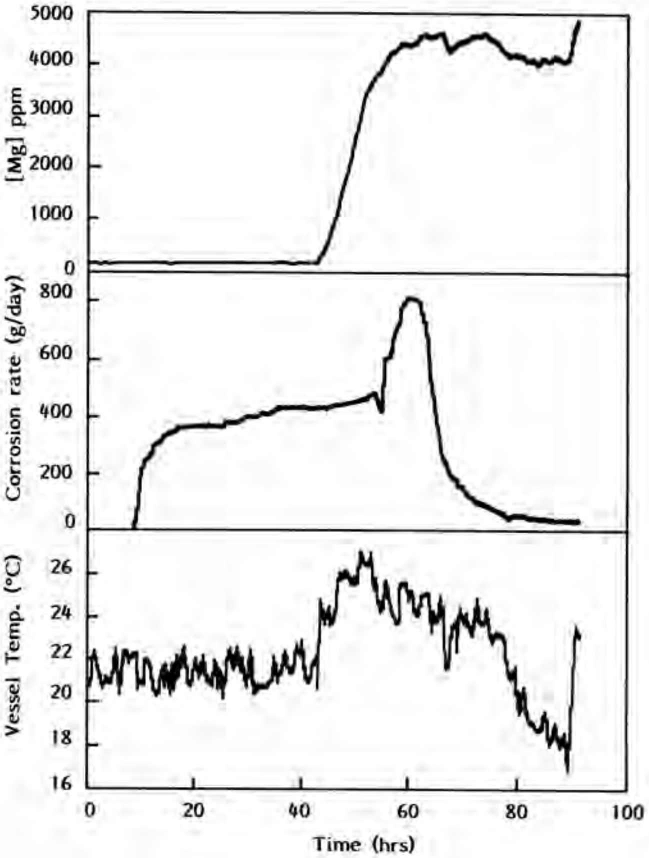

Fig. 5. 10 kg Scale Recirculation Test

The apparatus was operated for 40 hours in a once through manner. As Fig. 5. shows, the corrosion rate (as determined from the offgas hydrogen concentration) built up to a steady value of 350 g/day after a few hours operation. This rate then rose slowly to just over 400 g/day until the recycle pump was started 40 hours into the experiment. The dissolved magnesium concentration rose smoothly over the next 20 hours, eventually stabilising at 4500 ppm. The pH rose to 7.2, in good agreement with the theoretical solubility calculations (Fig. 1). The concentration was maintained at 4000 - 5000 ppm for a further 30 hours in order to determine if the system had any tendency to precipitate magnesium carbonate at these high Mg loadings. No precipitation was observed to occur in any portion of the circuit.

An experimental artefact is responsible for the reaction rate excursion shown in Fig. 5. When the recycle flow was started the cold town mains water supply was replaced with warm liquor from the dissolver vessel. The simple temperature control system took about 20 hours to restabilise the temperature of the experiment and a 5 C rise from 21 to 26 C occurred. As discussed above, this resulted in an increase in the underlying chemical rate and this is reflected in Fig. 5. As the temperature system regained control the rate decreased, but the dominant cause of the fall in rate to virtually zero (20 - 30 g/day) was inhibition of the corrosion reaction by dissolved product.

RESPONSE TO SIMULATED FAULT CONDITIONS

The response to, and subsequent recovery from, potential fault conditions is of considerable importance in any chemical process for the treatment of radioactive wastes. The temperature dependence of the carbonate process has already been discussed. The most likely fault on a real system would be the interruption of one or more reagent supplies. Interruption of water merely results in the draining of the debris heap and cessation of reaction. Interruption of CO_2 is potentially more serious, especially when operating at high magnesium loadings, because the gas desorbs from solution and precipitation of $MgCO_3$ can occur. Under normal operating conditions the carbonate system has a considerable built in buffering capability. The inverted 'V' shape of the solubility curve (Fig. 1) means that a dissolution operating on the low pH side can withstand considerable CO_2 loss before the pH rises to a point where precipitation will occur. This buffering capability falls as the magnesium loading rises.

An experiment was mounted to investigate the response of a dissolution to a drastic interruption of CO_2 supplies. A magnesium concentration of 3500 ppm was produced in the large vessel using liquor recirculation. CO_2 supplies were then switched off and the response of the process observed. After 10 minutes the liquid contents became slightly turbid as the pH rose from 6.9 to 7.8 (Fig. 6). The opacity of the solution continued to increase until, after 1 hour, it became impossible to look through the glass clarifier. After 20 hours running the spray head filter blocked and the feed and recycle pumps tripped. The vessel cooled and the temperature controller attempted to compensate by heating the contents of the header tank to 50 C, at which point the immersion heater trip activated. This resulted in considerable precipitation of $MgCO_3$ in the top tank. 70 hours after the initiation of the fault the settling tank contained a layer of white crystalline material that was about 0.1 m deep. This consisted almost entirely of $MgCO_3$. The contents of the dissolver vessel were also liberally coated with this material. The pH of the dissolver rose to peak value of 9.3 (Fig. 6) whilst that of the clarifier, where less CO_2 loss occurred, peaked at 8.2. The liquor magnesium loading fell from 3500 to 1100 ppm and the corrosion rate (H_2 basis) fell almost to zero, as expected.

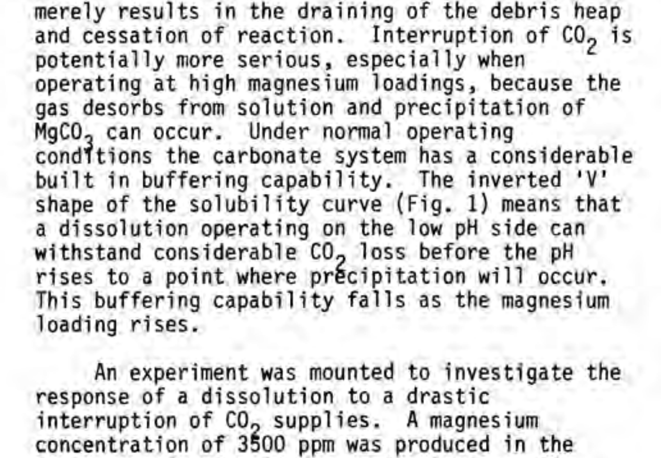

Fig. 6. pH During Simulated Fault Condition.

After clearing blocked filters and lines, the experiment was restarted. The magnesium loading dropped sharply as stagnant liquor was flushed through the apparatus. It then climbed sharply to 2400 ppm when the bleed system was started in order to maintain a 2000 ppm Mg loading. On restart, settling tank and vessel pH values immediately dropped to the usual operational value of about 6.7 (Fig. 6). Temperatures in the system soon returned to normal. The corrosion rate stabilised at 290 g/day. In addition to dissolution occurring on the Magnox heap subsequent Mg pickup from precipitated $MgCO_3$ took place in the settling tank. It is estimated from hydrogen concentration data that about 500 ppm of the total magnesium loading came from the setting tank with the balance coming from the heap. The deposit level in the settling tank fell slowly over the following week until it all re-dissolved. This process could have been accelerated by agitation of the settling tank contents or bypassing the debris heap so that the incoming reactant had a lower Mg loading. Thus, a spray dissolution can be operated at a high magnesium concentration even when recovering from a fault condition.

DISCUSSION

The objective of the work described in this paper was to obtain basic chemical information about the spray dissolution process. No unexpected difficulties were encountered during the experiments. A very simple method was shown to be effective in carbonating the process water. The corrosion rates that were obtained were generally lower than those in a submerged dissolution [1] but were large enough to clear the contents of a typical vault well within the nominal 1000 day period. Economic considerations of the effluent treatment plant throughput are likely to set dissolution time periods to around 1000 days whereas reaction rate data indicate that periods of about 100 days are technically feasible. The process chemistry displayed an inherent self *limiting* behaviour due to the fall in CO_2 solubility with temperature and inhibition of the reaction by high dissolved magnesium concentrations. Spray dissolutions are robust to interruptions of one or more process supplies. The most serious potential interruption would be to the CO_2, but the inherent buffering capability of the carbonate chemistry means that precipitation only occurs slowly. Moreover, the precipitated material can be readily dissolved at a later date. The low reactant inventory of the spray method is of assistance here - only a relatively small amount of magnesium containing liquor is present compared to that of a batch submerged system. In practice, therefore, only a limited amount of $MgCO_3$ precipitate, originating from liquor drained from the debris heap, would require to be re-dissolved after a process fault. The hydrogen production potential is governed by the carbon dioxide inventory and the rate of purging. The decrease in reaction rate is proportional to the fall in CO_2 partial pressure.

The water utilisation in these experiments was relatively poor when compared to that obtainable from a batch submerged dissolution. This is because the residence time of the carbonic acid reactant cannot be controlled but is determined by gravity and the geometry of the debris pile. However, real debris vaults are somewhat deeper than the 1 m depth scale used in these experiments. The recirculation data shown in Fig. 5 are replotted in terms of an effective bed depth in Fig. 7.

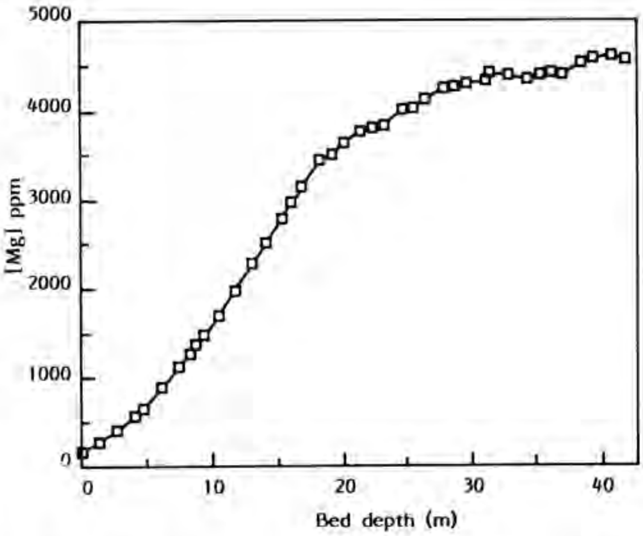

Fig. 7. Effect of Bed Depth on Magnesium Pick Up.

This permits the extrapolation of the data to allow the estimation of the outlet magnesium concentration that could be expected from a typical debris store. For a 5 m deep bed 800 ppm could be expected whilst for a 10 m bed this rises to about 1500 ppm. The ideal value for the optimum sizing of an effluent treatment plant would be 2000 ppm. Thus, recirculation of liquor to the top of the vault is an option that would need to be considered on a real plant. It would almost certainly be required towards the end of the process when the level of debris had fallen significantly. Much would depend upon the amount of effluent conditioning needed. If the extrapolation of Mg pickups to typical bed depths is low it will only influence the point at which recirculation is required. If the achieved loadings are in excess of those predicted by as much as a factor of two, the results obtained here show that no problems of dissolution and subsequent reprecipitation will be encountered. The inherently self limiting nature of the process, whereby reaction rate falls off as [Mg] increases, means that outlet concentrations much in excess of 2000 ppm are very unlikely on a real vault (Fig. 5).

The residues of the dissolution do not seem to pose any serious handling problems. The simple approach described above was sufficient to protect sensitive parts of the apparatus, but careful design would be needed for an active facility. The residues arisings in this study were almost entirely due to hardness in the mains water and their volume would have been considerably reduced if demineralised water had been used.

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