INFORMATION ON COORDINATED RESEARCH PROJECT: BEHAVIOURS OF CEMENTITIOUS MATERIALS IN MULTIPURPOSE PACKAGING FOR TRANSPORTATION, LONG TERM STORAGE AND DISPOSAL

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Abstract

The durability of concrete is an important issue and the imaging thereof plays a major part in the understanding of the characteristics of concrete. The ability of concrete to withstand the penetration of liquid and oxygen contribute to the durability of concrete. The durability of concrete, can in turn, be quantified by certain characteristics such as the porosity, sorptivity and permeability. For non-destructive analytical quantification of these parameters, neutron radiography was developed and validated against conventional measurements. Results indicated that because the neutron attenuation of the concrete and water differs to a significant degree, the movement of water in concrete (sorptivity) could be visualized. The neutron radiography results were validated against conventional measurements and excellent correlation was found. To improve the characteristics of current grout/cement matrixes used for the encapsulation of radioactive waste, different cement mixtures Cem 1 (96% OPC) and Cem 5 (mixture of 20% fly ash, 20% blast furnace slag and 60 % cement powder) with the addition of different admixtures, inert fibre material and plasticizers were investigated. With no formal guidance from the WAC of the disposal site, it was decided that the following matrix requirements have to be met in order to qualify a possible matrix for radioactive waste immobilisation research: -Total porosity less than 10 % (Implies a compression strength higher than 50 MPa) and -Sorptivity rate lower than 2.5 g/h (Implies pore structure not interlinked). Results with radioactive waste (excluding organic waste) indicated an admixture of bitumen or asphalt in CEM 1 (96% OPC cement) has the best characteristics and comply with the specified requirement. Treatment of contaminated organic waste which is a non standard waste stream proved to be difficult and direct disposal is also not an option because many organic liquids are immiscible. Cementation is generally not an option as the cement matrix binds poorly with the organic phase. The absorption of organics such as TBP and oil onto Nochar polymer systems has been demonstrated to be successful with no loss in activity. It has also been demonstrated that after the encapsulation of the polymer (absorbed with organics such as oil or TBP) into the selected cementitious grout, no leaching of radionuclides were observed. The tensile and compression strength of this matrix was improved with the addition of PVA fibres. In this research the effectiveness of chemically bonded phosphate ceramic (CBPCs) stabilisation technologies as alternatives to conventional waste immobilisation technologies was investigated for the immobilisation of ^{129}I (using ^{131}I as a surrogate) and ^{14}C. Performance tests (sorptivity, porosity and leaching tests) were used to determine waste-form durability. The results of this research indicate that the properties of the CBPC waste-forms when compared to the current cement matrix used at Vaalputs are superior. Excellent retainment of iodine in the phosphate ceramic matrices was observed using the ANSI/ANS 16.1 leaching procedure tests, yielding an effective diffusivity rate as low as 10^{-15} cm^2s^{-1}. The excellent performance results of the newly created Zn-P ceramic as an anionic radionuclide immobilisation waste-form implies that this waste-form may also be considered for other “problematic” radionuclides such as ^{99}Tc, ^{14}C and ^{36}Cl.

1. INTRODUCTION/BACKGROUND

Vaalputs is a national, near-surface, radioactive waste management facility that serves South Africa’s needs for disposal of low- and intermediate-level short-lived, radioactive waste generated by the nuclear, industrial, medical and agricultural sectors. The disposal of radioactive waste from Koeberg Nuclear Power Station at Vaalputs is currently carried out by means of a multiple-barrier concept using sulfate-resistant concrete containers. Results indicted that the geochemistry environment has a negative impact on the durability of the designed containers. The current backfill induces metal corrosion and chloride diffused into concrete paste. The formation of hairline cracks was also observed in the waste containers due to resin expansion in the waste matrix exerting pressure on the outer surface. These facts, as well as a shortage of specialized aggregate, indicated that the current waste container specifications were not adequate for the Vaalputs environment and that the current design, development, implementation and control of waste container specifications needs to be redefined with international standards as guideline.

2. OBJECTIVE

Kozak [1] indicated that the overall performance of the disposal system at the Vaalputs disposal site is rather insensitive to the longevity of the concrete containers. However, as the containers provide important operational safety functions, a program was initiated in 2003 to research new cement mixtures, grout compositions and container structures in order specify minimum requirements for future durable waste containers that will be applicable to all radioactive waste generators in South Africa that will be applicable to the geochemistry of the disposal site. The final technical specifications will be based on international standards with the minimum expected life span of the containers to be 300 years.

3. RESEARCH METHODOLOGY

Durability, in general, can be defined as the ability of a material to remain serviceable for at least the required designed lifetime [2]. The durability of concrete waste containers will decrease due to different degradation mechanisms, resulting in a gradual decrease in the ability to isolate waste from the surrounding geology. As degradation increases over a time period the permeability of water and surrounding chemicals from backfill into the cement paste will increase. The possible durability of concrete can therefore be quantified by determining parameters such as porosity, sorptivity and permeability of the initial cement paste. The porosity and sorptivity tests may be defined as techniques that measure the early age resistance of concrete to the transport of fluids through concrete. The purpose of the tests is not to determine absolute or intrinsic material characteristics, but to produce reliable values to be used for comparative purposes during the study. The rate of flow of liquids in porous media depends not only on the porosity, but also on the size and degree of continuity of the pores. The porosity of a concrete sample is an indication of the amount of voids in the concrete matrix. These pores are normally empty in dry conditions but can fill up when liquids are forced into them. The dominant mechanism controlling rates of water penetration into unsaturated or partially saturated concrete is absorption, caused by the capillary action of the concrete's pore structure. Sorptivity is then defined as the rate of movement of a waterfront through a porous medium under capillary action [3].

Cementitious research at Necsa for cement containers and grout matrixes were planned as follows:

- Develops analytical techniques for cement/grout studies
- Subject different manufactured cement and grout matrixes to porosity and sorptivity analysis for a first order selection.
- Specify new cement composition including admixtures for waste containers
- Design a new waste container that could accommodate stresses induces from waste matrix
- With selected grout matrixes radioactive waste were encapsulated and by determining the leaching properties a final selection was made.

All experimental methodologies, equipment, chemicals and results obtained are part of the laboratory that functions in accordance with processes that were drafted in line with ISO 9001 and implemented in the laboratory and final proposed cement structures (designed for the geochemistry of Vaalputs) was measured against international standards to ensure compatibility.

4. DESCRIPTION OF THE EXPERIMENTAL TECHNIQUES AND EQUIPMENT

The porosity and sorptivity tests may be defined as techniques that measure the early age resistance of concrete to the transport of fluids through concrete. The purpose of the tests is not to determine absolute or intrinsic material characteristics, but to produce reliable values to be used for comparative purposes during this study.

4.1. Measurements by neutron radiography (NRad)

Neutron radiography (NRad) is a useful, non-destructive method for determining hydrogen content in various materials [4]. Hydrogen content in samples is determined by quantitative analysis of measured profiles of neutron attenuation in the samples. Thermal neutrons are attenuated (mostly scattered) to a significant degree by hydrogen, and substances that contain hydrogen. Thus, neutron images of porous media containing water can provide an accurate indication of the pore structure of the media.

To obtain quantitative neutron data, the South African Neutron Radiography (SANRAD) facility at the SAFARI-1 Nuclear Research reactor, operated by Necsa, was used [5]. The quantitative data are presented as a digital image via a CCD-camera and from these radiographs the analysis are performed.

4.1.1. Porosity measurements

After the conventional porosity test, the samples are prepared for neutron radiography testing. They were completely dried in an oven, and the neutron radiography image captured (I_{Dry}). The samples were treated in the same way as for the conventional measurement but the saturated concrete was then put into the neutron beam at exactly the same geometry as before to capture the saturated neutron image (I_{Wet}). Water calibration was performed as described by Middleton et al. [6], the average intensities of both radiographs measured. The porosity was calculated by [7]:

$$\text{Porosity (\%)} = \frac{\mathrm{In}(I_{Sat}/I_{Dry})}{h\rho_w\mu_w} \quad \text{...} (1)$$

where h is the thickness of the specimen in cm, $\underline{\mu}_{\mathrm{w}}$ is the thermal neutron attenuation of water obtained for the specific specimen geometry in cm^2/g and $\underline{\rho}_{\mathrm{w}}$ is the density of water in $\mathrm{g/cm}^3$.

4.1.2. Water sorptivity tests

For neutron radiography tests, the samples were covered on the sides except on the bottom with aluminium tape to prevent water flow from the sides into the concrete. The neutron image was taken for the dry sample. They were placed in 5 mm water for water to be sucked by capillary action into the concrete from the bottom only. After 10, 30, 60 and 120 min each sample was taken from the water to be radiographed and then placed back into the container to saturate for another period of time after radiography.

4.2. Gravimetrical analysis

4.2.1. Porosity measurements

The preparation of the sample for the porosity test was the same as for the permeability test. The remaining two of the five core slices were used for the porosity test. After drying, the discs were measured and weighed to obtain their density, subjected to a vacuum for 1 hour to ensure that all the air was removed, saturated with water under the vacuum and subjected to vacuum for another hour. After another hour in water to ensure all the air was removed, they were weighed to obtain their saturated mass. Since porosity is a function of the percentage weight gain and the density of the sample, the following equation was used to calculate the total porosity of the samples:

$$n = \frac{M_{SW} - M_{s0}}{Ad\rho_w} \qquad (2)$$

where:

M_{sw} = the vacuum saturated mass of the specimen determined in section 5(n) to the nearest 0.01g.

M_{s0} = mass of the specimen at t=0 to the nearest 0.01g.

A = cross-sectional area of the specimen to the nearest 0.02mm^2.

d = average specimen thickness to the nearest 0.02mm.

ρ_w = density of water = 1kg/m^3

4.2.2. Water sorptivity tests

Sorptivity can be calculated from measurements of the penetration depth of water. Sorptivity tests was were conducted in a room in which the temperature is controlled at 23 ± 2ºC. The thickness of the oven-dried cubes was measured with the Vernier and the dry mass was recorded. In order to ensure the movement of a front of water through the specimen in one direction, sealant was added around the vertical edges of the specimens, without blocking any part of the horizontal test face whatsoever.

Any of the following can be used:

- Epoxy paint (e.g. ABE Epidermix 365 or Sikaguard Wetseal A+B)
- Packaging tape
- Vacuum grease
- Epicon grease

The cubes were placed in a plastic tray and distilled water was poured into the tray until a water level was reached that was 2 mm above the horizontal test face.

Periodically, the matrix specimen was removed; excess water wiped off the surface, and then weighed to the nearest 0.01 gram. After recording the mass, the cube was immediately returned to the water. The measurement was done for a period of three days. The mass increase due to capillary action was plotted against the square root of time as indicated in Figure 1.

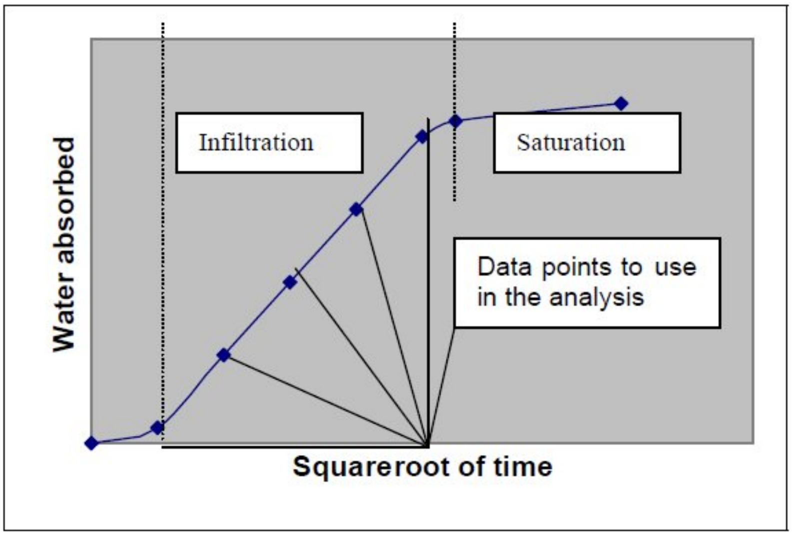


FIG. 1. Relationship between mass increase and square root of time.

The sorption coefficient, A [kg/(m^2×$s^{½}$)] can then be determined from the slope of the line of best fit by linear regression analysis

4.3. Determination of the effective diffusivity (leaching) of radionuclides from grout matrixes

For this report, the American Nuclear Society leaching test method by American national Standards Institute (ANSI/ANS-16.1) was used. In the test method (1) the leachate used is demineralised water and is continually changed at time intervals 24, 48, 72 and 96 hrs. The leachate is kept at the temperature range between 17.5° C and 27.5° C for the duration of the test. The ratio of the leachant volume to the specimen external geometric surface area is maintained within fixed bounds (10 ± 0.2 cm) during the leaching interval. Under these conditions the mass transport equation permits the calculation of effective Diffusivity. If less than 20% of a leachable species has been removed by the time t=$\sum(\Delta t)$n, the effective Diffusivity can be calculated by the formula

$$D = \pi\left[\frac{a_n/A_0}{(\Delta t_n)}\right]^2 \left[\frac{V}{S}\right]^2 T \qquad (3)$$

where:

D = Effective Diffusivity (cm^2/s)

a_n = amount of species leached from the specimen during the n-th leaching Interval (counts/5min)

A_o = amount of species in the specimen at the beginning of the first leaching (Counts/5min) interval

Δt_n = duration of the n-th leaching interval

V = Volume of cement sample

S = geometric surface area of the specimen as calculated from measured dimensions, cm^2, and

$$T = \left[\frac{1}{2}\left(t_n^{1/2} + t_{n-1}^{1/2}\right)\right]^2 \qquad (4)$$

If twenty percent or more of a leachable species has been removed by time t, the Effective Diffusivity can only be calculated from a shape-specific solution of the transport equation.

4.4. Manufacture of matrix/cement cubes using different cement mixes

The pozzolanic cement materials (CEM 1 and CEM 5) were sourced from Portland Cement (OPC) in Pretoria, Ash Resources (Fly Ash) in Randburg and Blast Furnace Slagment from Iscor in Vanderbijlpark. The mineral compositions of the different cement mixtures are indicated in Table 1. These different mixtures were used in conjunction with cement extenders (Si fume, Asphalt, bitumen, Attapulgite, vermiculite, etc.) to manufacture to determine the influence of cement extenders on the physical properties of matrix structures.

TABLE 1. SPECIFICATIONS OF MIXTURES USED FOR ALTERNATIVE CEMENT CONTAINERS

	CEM 1 OPC*	CEM 5 OPC**
SiO_2	19 – 24%	32%
CaO	63 – 68%	47%
S		0.2%
SO_3		0.1%
$Al2O_3$	4 – 7%	12.4%
MgO	0.5 – 3.5%	2.9%
FeO		0.1%
Fe_2O_3	1 – 4%	3.2%
Mn_2O		0.2%
Mn_2O_3		0.4%
P_2O_2		
P_2O_5		0.2%
K_2O	0.658%	0.5%
NA_2O	0.2 – 0.8%	0.5%
TiO_2		0.5%

*CEM 1 Ordinary Portland Cement: 96% OPC cement, 4% fly ash.
**CEM 5 Portland Cement: 40% OPC, 30% blast furnace slag and 30% fly ash.

5. RESEARCH RESULTS

5.1. Development of waste container

The initial waste containers disposed at Vaalputs are types C1, C2, C3 and C4 concrete drums that have varying inside diameters resulting in different wall thicknesses [8] and are used for packaging and disposal of ILW (Table 2). The drums are reinforced with 6-mm steel bar and may have a gross mass of up to 6 300 kg. Concrete drums are often used in conjunction with an inner metal liner that contains the waste matrix (Fig. 2). The drums are custom manufactured according to a prescribed specification and the manufacturing process is subject to strict quality control measures [8].

TABLE 2. DIMENSIONS OF CONCRETE DRUM TYPES C1, C2, C3 AND C4

Drum Type	Length (m)	Outside diameter (m)	Inside diameter (m)	Wall thickness (mm)	Reinforcing bar (mm)
C1	1.3	1.4	1.08	160	6
C2	1.3	1.4	0.778	310	6
C3	1.3	1.4	0.59	405	6
C4	1.3	1.1	0.78	160	6

The specific composition of the Portland cement used during manufacturing is specified to be sulfate-resistant concrete [9]. This cement has a very low (C_3A) composition which accounts for its high sulfate resistance.

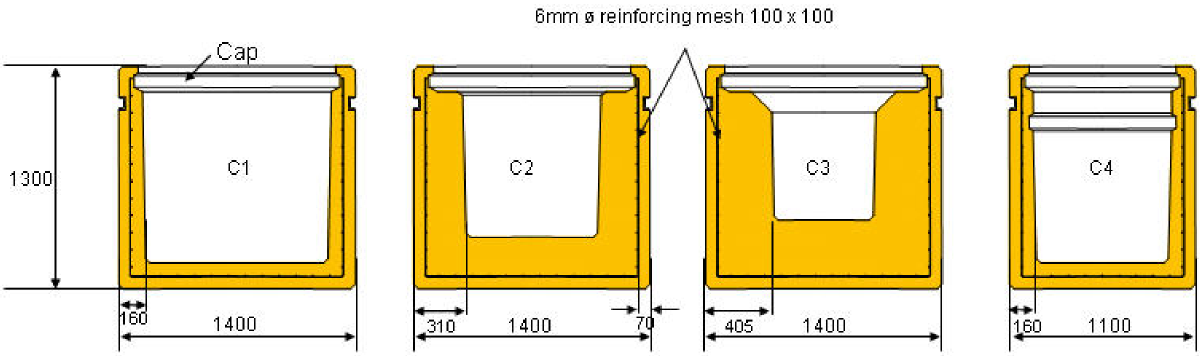


FIG. 2. *Cross sections of types C1, C2, C3 and C4 reinforced concrete drums (dimensions in mm) (after [8]).*

To determine the optimum concrete composition using South Afican availible source material different concrete samples were produced as indicated in Figure 3. These concrete blockd were cured under water for 28 days and subjected to compression and tensile strengths (Table 3). With the aid of NRAD technology the influence of different aggregates in the cement paste were investigated as indicated in Figure 4.

FIG. 3. Manufacturing of concrete cubes (cured for 28 days under water) for compression and tensile testing.

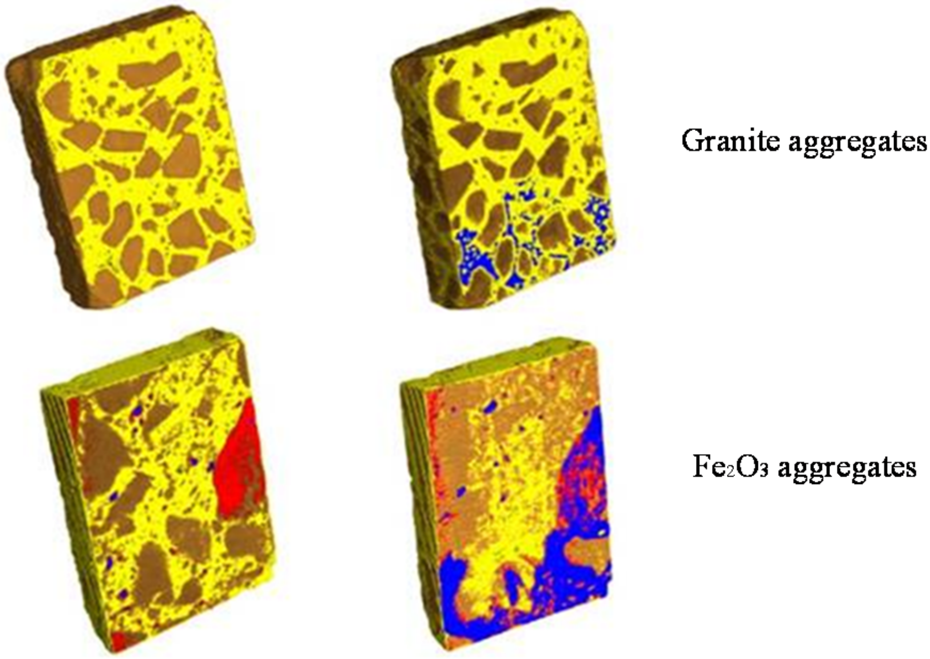


FIG. 4. Testing of the influence of aggregate used for concrete manufacturing by Nrad(water penetration study).

TABLE 3. CONCRETE PARAMETER DATA.

Parameters	Average International Specifications	Koeberg	Manufacture A	Manufacturer B
Comp.	Min 60 MPa	50 MPa	35 MPa	70-80 MPa
Tensile	Min 5 MPa	4.5 MPa	2.5 MPa	5.2-5.8 MPa
Density	Min 2 400 kg/cm^3	2 400 kg/cm^3	2 200 kg/cm^3	2 700 kg/cm^3
W/C Ratio	Less than 0.5	Less than 0.45	Less than 0.45	Less than 0.45
Porosity	Less than 12%	3%	20%	< 3%
Sorptivity	Less than 1.5 gram/hour	1.0 gram/hour	3.0 gram/hour	< 1.0 gram/hour

5.2. Development of grout matrix for encapsulation

5.2.1. Initial selection of grout matrixes

Waste package components are generally selected to provide a leach resistant matrix for contaminant immobilisation and mechanical stability and to resist void formation in the repository. In the current draft WAC (Waste Acceptance Criteria) for Vaalputs, it is recommended that only CEM 1 cement powder must be used for waste packages. CEM 1 cement implies 98% pure cement. To improve the leaching resistance of the grout matrixes manufactured with CEM 1 and CEM 5 OPC (Ordinary Portland Cement) powder, different percentages of various admixtures were added to these cement powders to manufacture grout cubes (matrices). To enhance the characteristics of these cement/grout mixtures, inert fibre material and plasticizer were also added and studied.

The porosity and sorptivity characteristics of the matrices were compared to determine the best available matrixes to be used in conjunction with radioactive waste (next research aspect).

As the total porosity of the matrix is an indication of the amount of voids in a matrix and the lower the total porosity value of a matrix is, the higher is its compression and tensile strength. The initial selection was based on a cut-off value of 20% and lower. The matrixes that passed the initial total porosity selection were then re-selected on water sorption (Sorptivity) criteria. The sorptivity value is an indication of the average water movement through the matrix. This indirect measurement is done to determine whether the pore structure is interconnected, whereby a matrix structure with a high sorptivity rate will deteriorate much faster, because of dissolution reactions. This technique was used instead of the permeability technique that is time consuming. However, leaching rates with radioactive waste will be performed on selected matrixes. As no information is available in literature regarding water movement through grout matrixes, a cut-off value of 2.5 g/h and lower was arbitrarily chosen.

With no formal guidance from the WAC of Vaalputs, it was decided that the following matrix requirements have to be met in order to qualify a possible matrix for radioactive waste immobilisation research:

1. Thermal stability between 5ºC and 65ºC (Temperature fluctuations at Vaalputs);

2. Total porosity less than 20% (Implies a compression strength higher than 5 MPa);

3. Sorptivity rate lower than 2.5 g/h (Implies pore structure not interlinked and that leaching is less than 10^{-6} g /l).

The average experimental results per cement/grout class are summarised in Table 4 (for CEM 5 matrixes) and Table 5 (CEM 1 matrixes). The results indicate that the best matrix currently to be investigated further for waste immobilisation is an admixture of bitumen or asphalt in OPC cement.

TABLE 4: AVERAGE RESULTS FOR CEM 5 CEMENT/GROUT MATRICES

Initial OPC Matrix mixture 15% BFS, 15% FA, 60% OPC	Total Porosity of matrix	Sorptivity rate (grams/hour)	Comment
With added			
Attapulgite	51%	21.4	Not selected: high capillary suction
Silica gel	40%	6.8	Not selected: high capillary suction
Silica gel and fibres	51%	14.1	Not selected: high capillary suction
Silica gel and plasticiser	47%	10.2	Not selected: high capillary suction
Fly ash	35%	9.2	Not selected: high capillary suction
Fly ash and fibres	40%	6.1	Not selected: high capillary suction
Fly ash and plasticiser	26%	3.8	Not selected: high capillary suction
Vermiculite	32%	5.8	Not selected: high capillary suction
Vermiculite and fibres	45%	3.2	Not selected: high capillary suction
Vermiculite and plasticiser	32%	1.7	Not selected: high capillary suction
BFS (blast furnace slag)	28%	6.1	Not selected: high capillary suction
BFS and fibres	33%	5.1	Not selected: high capillary suction
BFS and plasticiser	25%	4.2	Not selected: high capillary suction
Silica fume	25%	6.2	Not selected: high capillary suction
Silica fume and fibres	33%	4.2	Not selected: high capillary suction
Silica fume and plasticiser	40%	4.5	Not selected: high capillary suction
Lime	28%	2.8	Not selected: high capillary suction
Lime and fibres	24%	7.2	Not selected: high capillary suction
Lime and plasticiser	19%	2.8	Not selected: high capillary suction
Asphalt	25%	3.1	Not selected: high capillary suction
Asphalt and fibres	24%	4.5	Not selected: high capillary suction
Asphalt and plasticiser	20%	1.7	Recommended matrix
Bitumen	15%	3.1	Not selected: high capillary suction
Bitumen and fibres	15%	1.7	Recommended matrix
Bitumen and plasticiser	18%	1.4	Recommended matrix

TABLE 5: AVERAGE RESULTS FOR CEM 1 CEMENT/GROUT MATRICES

Initial OPC Matrix mixture 96% OPC	Total Porosity of matrix	Sorptivity rate (grams/hour)	Comment
With added			
Silica fume	25%	10.2	Not selected: high capillary suction
Silica fume and fibres	33%	5.5	Not selected: high capillary suction
Silica fume and plasticiser	26%	4.2	Not selected: high capillary suction
BFS (blast furnace slag)	25%	11.7	Not selected: high capillary suction
BFS and fibres	27%	7.2	Not selected: high capillary suction
BFS and plasticiser	24%	7.2	Not selected: high capillary suction
Silica gel	25%	6.2	Not selected: high capillary suction
Silica gel and fibres	31%	8.1	Not selected: high capillary suction
Silica gel and plasticiser	31%	8.2	Not selected: high capillary suction
Lime	24%	6.9	Not selected: high capillary suction
Lime and fibres	25%	8.23	Not selected: high capillary suction
Lime and plasticiser	21%	6.9	Not selected: high capillary suction
Silica fume	25%	8.8	Not selected: high capillary suction
Silica fume and fibres	33%	5.2	Not selected: high capillary suction
Silica fume and plasticiser	26%	4.3	Not selected: high capillary suction
Fly ash	20%	6.5	Not selected: high capillary suction
Fly ash and fibres	20%	4.2	Not selected: high capillary suction
Fly ash and plasticiser	15%	4.2	Not selected: high capillary suction
Vermiculite	25%	2.8	Not selected: high capillary suction
Vermiculite and fibres	20%	7.7	Not selected: high capillary suction
Vermiculite and plasticiser	15%	3.7	Not selected: high capillary suction
Asphalt	20%	3.2	Not selected: high capillary suction
Asphalt and fibres	30%	4.3	Not selected: high capillary suction
Asphalt and plasticiser	18%	2.9	Not selected: high capillary suction
Bitumen	< 5%	< 1	Recommended matrix
Bitumen and fibres	< 5%	< 1	Recommended matrix
Bitumen and plasticiser	< 5%	< 1	Recommended matrix

5.2.2. Influence of radioactive waste on selected matrixes

Requirements of the IAEA TECDOC-285 Characteristics of radioactive waste forms conditioned for storage and disposal: Guidance for the development of waste acceptance criteria" (IAEA, Vienna, 1983) concerning waste acceptance criteria stipulate that the waste form (grout matrix and the radioactive waste stream) must be compatible, to ensure mechanical and chemical durability of the waste package. Radioactive liquids generated at Necsa are currently immobilised in a mixture of 50% vermiculite and 50% CEM 1 cement powder. To compare the use of the vermiculite-cement grout with alternative proposed matrixes, radioactive waste were encapsulated into a mixture of vermiculite-cement, asphalt-cement, bitumen-cement, silica fume-cement and blast furnace slag-cement grouts.

5.2.2.1. Encapsulation of Tritium waste

Although Portland cement may be the most economical material to bind HTO, cement is a monolithic, porous solid and a gradual release of Tritium can therefore be expected. The results in Table 5 indicated that the matrixes consisting of:

1. 30% Bitumen in 70% OPC
2. 30% Asphalt in 70% OPC

3. 30% Vermiculite in 70% OPC and
4. 50% Vermiculite in 50% OPC

increased the characteristics of the matrixes tremendously, as the combined selected criteria of 2.5 g/h for water penetration (rate of capillary suction is an indication of the dissolution of matrix) and effective diffusivity rate of radionuclides 1 10^{-3} cm^2/s (presents the migration of radionuclides through the matrix) were easily met for the encapsulated titrated water (30%). Although the effective diffusivity rate of the matrices manufactured with lime, silica fume and BFS were within specifications, the sorptivity rates were too high, indicating that these cubes will deteriorate, due to the dissolution of the grout matrix.

TABLE 5. CHARACTERISTICS OF DIFFERENT GROUT MATRIXES

Admixture	**% Admixture**	**Sorptivity (g/h)**	**D** (cm^2/s)
Vermiculite	50	2.312139	1.1E-10
Vermiculite	30	2.312139	2.0E-10
Asphalt	30	2.312139	3.4E-10
Bitumen	30	0.578035	3.5E-10
Lime	10	5.780347	2.0E-10
Silica Fume	30	4.624277	1.5E-10
BFS	30	2.890173	3.7E-10

To enhance the properties of the tritiated waste forms, the surface of the grout cubes were subjected to different coatings.

TABLE 6. CHARACTERISTICS OF DIFFERENT COATING APPLIED TO SELECTED GROUT MIXTURE.

Admixture	Uncoated	**Bitmen**	**Epoxy tar**	**Sasol wax**
Bitmen	3.5E-10	6.0E-14	6.1E-13	2.1E-12
30% V	2.0E-10	8.0E-13	2.3E-12	1.2E-11
Asphalt	3.4E-10	1.4E-13	2.7E-13	1.2E-11

The results in Table 6 indicate that, with this additional barrier, all the cubes passed the selected criteria tests, as the water penetration could not be measured, and that the effective diffusivity rate for Tritium decreased three orders with the use of bitumen as coating. However, any damage to this applied barrier would not be catastrophic as the effective diffusivity rate through the matrixes without this added protection is within the proposed requirements of 1 10^{-3} cm^2/s.

The best matrix for the encapsulation of tritiated water (30%) was a mixture of 30% Bitumen in 70% OPC, coated with a single surface application of bitumen liquid.

5.2.2.2. Encapsulation of inorganic waste containing radionuclides

A very limited cement encapsulation test program was conducted to prove the compatibility of the cementitious grout with different waste streams. Polymeric fibres were added as reinforcement into different grout pastes. The results in Table 7 indicated that the all the selected matrixes can be used for encapsulating up to 30% loading (by mass) into the cement grout.

TABLE 7. CHARACTERISTICS OF DIFFERENT WASTE STREAMS ENCAPSULATED IN SELECTED GROUT

10% Waste loading				
Waste type	Bitumen	SF	30% V	Asp
Graphite dust	3.0E-11	-	7.3E-11	3.6E-11
Sludge	1.1E-11	-	1.8E-13	2.4E-11
Chabazite	5.6E-13	-	-	5.6E-13
RF resin	2.8E-13	-	-	1.1E-13
20% waste loading				
Waste type	Bitumen	SF	30% V	Asp
Graphite dust	6.0E-11	-	2.5E-10	3.6E-11
Sludge	4.0E-11	-	5.9E-13	3.7E-11
Chabazite	6.8E-13	-	-	3.7E-13
RF resin	6.8E-13	-	-	2.5E-11
30% waste loading				
Waste type	Bitumen	SF	30% V	Asp
Graphite dust	2.8E-10	-	2.6E-10	6.8E-11
Sludge	1.4E-11	-	7.3E-13	6.8E-11
Chabazite	3.6E-13	-	-	1.4E-13
RF resin	3.2E-12	-	-	1.4E-13

5.2.2.3. Encapsulation of organic radioactive waste

Treatment of contaminated organic waste which is a non standard waste stream proved to be difficult and direct disposal is also not an option because many organic liquids are immiscible. Cementation is generally not an option as the cement matrix binds poorly with the organic phase. Encapsulating organic waste directly in cement is not feasible without pre-treatment with adsorbents [10]. Nochar's Petrobond and Acidbond are a group of 3rd generation polymers designed to solidify organics, sludges, acids, alkaline and aqueous radioactive waste into a solid matrix. The Imbiber Beads®, and Nochar® products are proprietary polystyrene polymeric materials and the aqueous solution spill stabilizers are derived from various processing modifications of polypropylene and polyacrylates [11]. Both Petroset® and Aquaset® materials are modified aluminosilicate minerals (Clays). Nochar polymer technology has been successfully deployed in the immobilization of waste oil by a number of non-UK nuclear facilities [12]. This technology was considered by British Nuclear Group as a potential innovative option to waste oil treatment and disposal, as it facilitates the conversion of a liquid waste stream into a solid polymer matrix which potentially opens new disposal routes such as burial at the Low Level Waste Repository (LLWR) at Drigg. Based on research results organic waste at Necsa is using a combination of treatment processes schematically presented in Fig. 6.

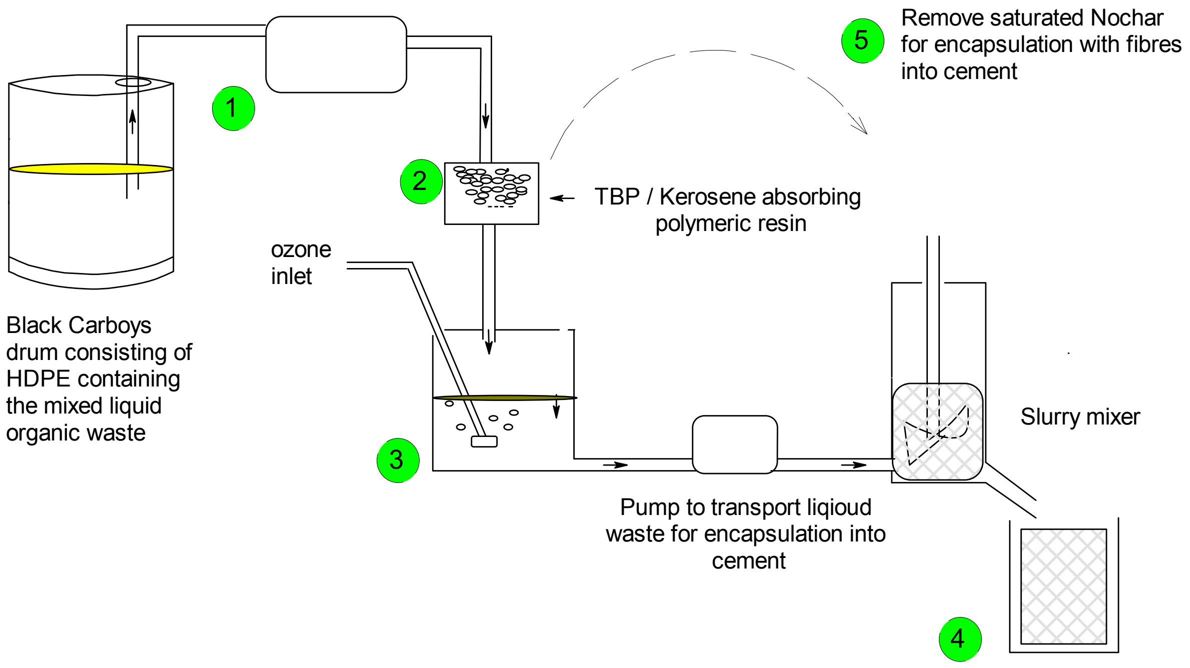
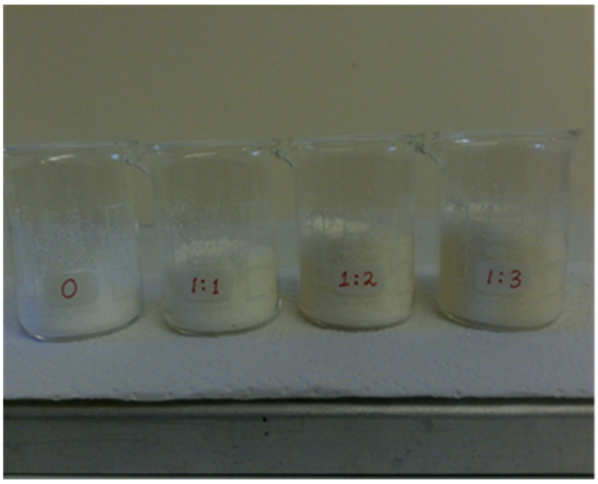
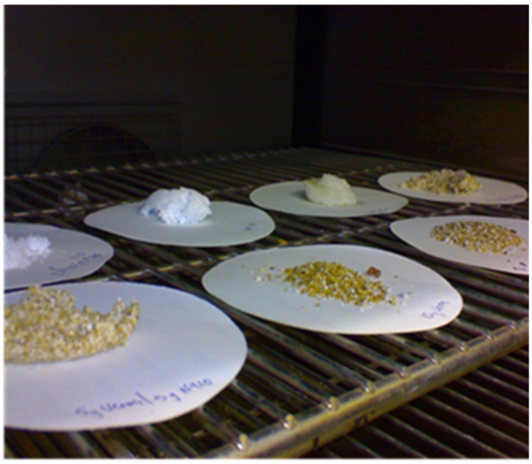


FIG. 6. A proposed diagram for the treatment of mixed liquid organic waste.

Results clearly confirm literature results that Nochar N910 polymer, can adsorbs up to three times the volume of organics (Fig. 7.). The stability of oil-absorbed Nochar into proposed CEM1-asphalt grout matrix of using PVA fibres as a binding agent, was studied.



TBP adsorption



Radioactive oil Adsorption

FIG. 7. Adsorption of organic compounds into different ratio's of Nochar Polyme.

A very limited cement encapsulation test program was conducted to prove the compatibility of the solidified TBP-Nochar polymer with cementitious grout. Polymeric fibres were added as reinforcement with the aim to anchor the Nochar resin into the cement. The polymeric fibres were polyvinyl alcohol (PVA supplied by Everite) and homo polyacrylic fibres (PAN supplied by Beier SA). These fibres are widely used in the building industry for cement reinforcement and may serve as a binding agent for Nochar, improving Nochar resin's encapsulation.

The results in Table 8 was used to construct the sorptivity plot as indicated in Fig. 1 by plotting the mass increase due to capillary action against the square root of time.

TABLE 8. INGRESS OF WATER INTO GROUT MATRIX

Time Hours	$(\text{Time})^{0.5}$ $\text{Hours}^{0.5}$	Mass (M_f) grams	Mass increase M_f-M_i (gram)
Start		57.7502	0
1	1	60.2521	2.5019
2	1.4	65.1330	7.3828
4	2	65.3961	7.6465
24	4.9	65.5260	7.7775

The sorption coefficient, A [$kg/(m^2 \times s^{½})$] of 2.5 $kg/(m^2s^{½})$ is lower than the value of value 3 $kg/(m^2s^{½})$ that are currently suggested for the WAC of Vaalputs (based on current disposed concrete waste containers) and are therefore acceptable for disposal at Vaalputs.

To determine leaching values from the matrixes, TBP – kerosene mixture were spiked with low level enriched uranium, absorbed into Nochar 910 and encapsulated in PPC cement. The water was chemically analysed with the GC-MS and UV VIS using the Bromo – Padap [2-(5-bromo-2-pyridylazo-)-5diethylaminophenol] method. No uranium above the detection limit of the analysis method (10 ppb) was measured. The cutting of the grout structure, Fig. 8, revealed a dense homogenously structure

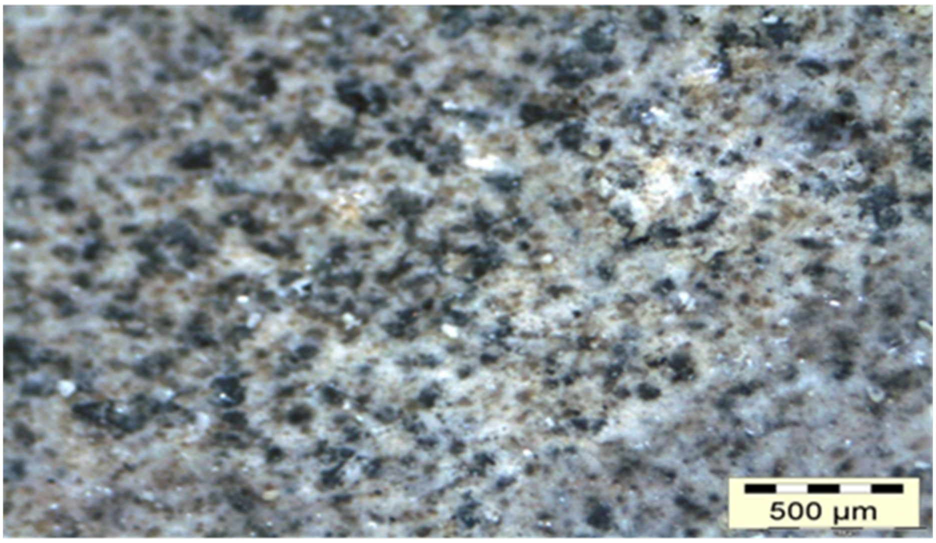


FIG. 8. Homogeneous grout structure.

As there were no positive uranium results to calculate the leaching rates, the experiment was repeated using oil spiked with radioactive Cs-137. The oil was absorbed onto Nochar at a ratio of 2:1 (oil to nochar) and the solidified matrix was packed into a test-tube as indicated in figure 9. Water was added to the top of this solidified matrix.

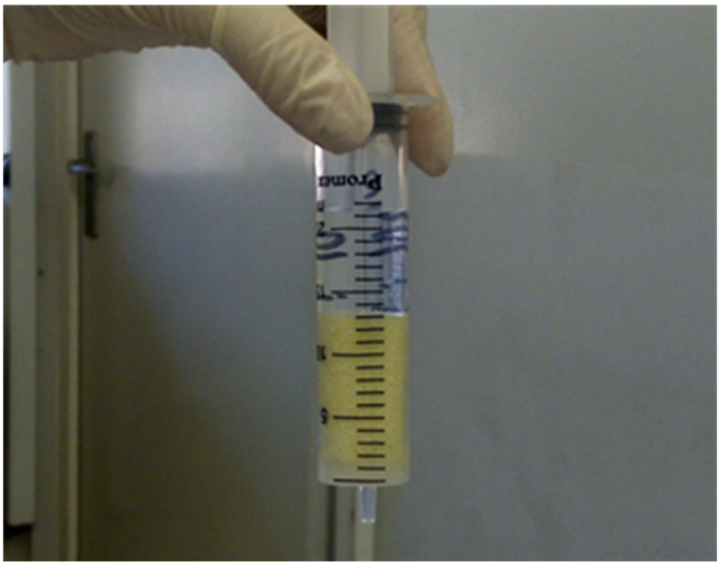


FIG. 9. Leaching studies of Cs-137 contaminated oil encapsulated into Nochar.

During the experimental procedure the water did not penetrate the solidified matrix and no water movement was observed under gravimetrical flow. After 5 days the water was measured for Cs-137 leaching and no Cs-137 was detected. In order to facilitate the experiment the water was forced through the solidified matrix by pressure and again in the collected water no Cs-137 was present. In order to be ultra conservative the experiment was repeated by crushing the solidified matrix and then to perform a batch leaching experiment in water over a period of 5 days. No Cs-137 could be observed.

This result indicated that:

- Absorbed oil in the structure of the polymer cannot be released even with free standing water;

- Cs-137 absorbed in oil, will not leach even in free standing water due to the water repelling nature of the oil /polymer complex; and

- All oil is solidified as a solid matrix and no unbounded oil is present in the pores of this solidified matrix.

As no Cs-137 leaching was observed during this ultra conservative approach, it implies that the contaminated oil is irreversible absorbed into the structure of the polymer and no leaching of radionuclides (Cs-137 representative) will occur when encapsulation this adsorbed polymer into grout.

5.2.2.4. Encapsulation of radioactive waste containing for ^{99}Tc, ^{129}I and ^{137}Cs

Although cement-based waste-forms have been proven to be successful in many radioactive waste solidification applications, some leaching problems exist and limit the usefulness of cement (grout) solidification for ^{99}Tc, ^{129}I, ^{14}C, ^{137}Cs e.t.c. encapsulation. Different cold ceramics samples were manufactures as indicated in Table 9.

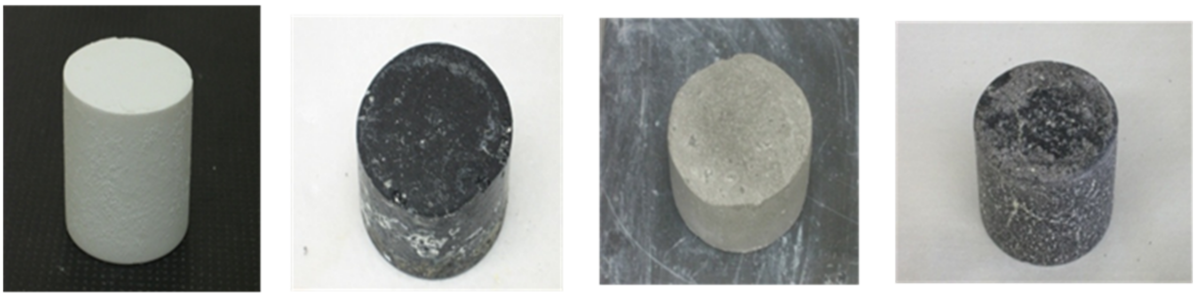
TABLE 9. MANUFACTURING OF DIFFERENT COLD CERAMIC TEST SAMPLES

MATRIX	STARTER POWDERS	SOLUTION
Magnesium potassium phosphate (MKP)	MgO, H_3BO_3, KH_2PO_4, fly ash	Water
Iron phosphate (FeP)	Fe_3O_4, H_3BO_3, fly ash	H_3PO_4
Zinc phosphate (ZnP)	ZnO, fly ash	Al/Zn buffered H_3PO_4
Calcium phosphate (CaP)	CaO, fly ash	Al/Zn buffered H_3PO_4
Aluminium phosphate (AlP)	Al_2O_3, fly ash	H_3PO_4
Iron-magnesium phosphate (Fe-Mg)	MgO, Fe_3O_4, H_3BO_3, fly ash	H_3PO_4
Zinc-magnesium phosphate (Zn-Mg)	ZnO, Fe_3O_4, H_3BO_3, fly ash	H_3PO_4
Calcium-magnesium phosphate (Ca-Mg)	CaO, Fe_3O_4, H_3BO_3, fly ash	H_3PO_4

The results regarding the sorptivity (water penetration) and porosity values indicated in Table 10 and Figure 10 demonstrate that cold ceramic matrixes manufactured at room temperature can be considered for encapsulation. In order to determine the leaching capabilities of these matrixes, 1 MBq of different radionuclides were encapsulated into these selected matrixes for evaluation.

TABLE 10. CHARACTERISTICS OF DIFFERENT MANUFACTURED COLD CERAMIC MATERIALS.

MATRIX	SORPTIVITY (grams/hour)	TOTAL POROSITY (%)
MKP	0.82	0.13
FeP	1.30	0.13
ZnP	0.57	0.08
Fe-Mg (1:1)	0.19	0.15
Fe-Mg (2:1)	0.41	0.05



MKP FeP ZnP Fe-Mg 1:1

FIG. 10. Examples of different cold ceramic matrixes.

The results of the leaching tests done on the selected cold ceramic matrixes indicated in Table 11 that all matrixes can be considered for encapsulation. However the FeP matrix with 30 % flyash seems to perform slightly better.

TABLE 11. LEACHING RESULTS FROM MANUFACTURED COLD CERAMIC

MATRIX	% FLY ASH	^{60}Co LEACHING RATE (cm^2/s)	^{131}I LEACHING RATE (cm^2/s)
MKP	0% fly ash	5.96×10^{-12}	1.76×10^{-12}
	30% fly ash	1.60×10^{-12}	6.26×10^{-13}
FeP	0% fly ash	8.91×10^{-13}	6.59×10^{-12}
	30% fly ash	4.13×10^{-14}	6.74×10^{-14}
ZnP	30% fly ash	9.45×10^{-11}	8.29×10^{-13}
Fe-Mg (1:1)	0% fly ash	9.76×10^{-9}	7.56×10^{-9}
	30% fly ash	1.97×10^{-9}	5.37×10^{-8}
Fe-Mg (2:1)	0% fly ash	1.20×10^{-11}	9.33×10^{-11}
	30% fly ash	4.0×10^{-12}	6.12×10^{-12}

6. DISCUSSION

To improve the characteristics of current grout/cement matrixes used for the encapsulation of radioactive waste, different cement mixtures CEM 1 (96% OPC) and CEM 5 (mixture of 20% fly ash, 20% blast furnace slag and 60 % cement powder) with the addition of different admixtures, inert fibre material and plasticizers were investigated. With no formal guidance from the WAC of the disposal site, it was decided that the following matrix requirements have to be met in order to qualify a possible matrix for radioactive waste immobilisation research:

- Total porosity less than 10 % (Implies a compression strength higher than 50 Mpa) and
- Sorptivity rate lower than 2.5 g/h (Implies pore structure not interlinked)

Results with radioactive waste (excluding organic waste) indicated in Table 12 that an admixture of bitumen or asphalt in CEM 1 (96% OPC cement) has the best characteristics and comply with the specified requirement.

Treatment of contaminated organic waste which is a non standard waste stream proved to be difficult and direct disposal is also not an option because many organic liquids are immiscible. Cementation is generally not an option as the cement matrix binds poorly with the organic phase. The absorption of organics such as TBP and oil onto Nochar polymer systems has been demonstrated to be successful with no loss in activity. It has also been demonstrated that after the encapsulation of the polymer (absorbed with organics such as oil or TBP) into the selected cementitious grout, no leaching of radionuclides were observed. The tensile and compression strength of this matrix was improved with the addition of PVA fibres.

In this research the effectiveness of chemically bonded phosphate ceramic (CBPCs) stabilisation technologies as alternatives to conventional waste immobilisation technologies was investigated for the immobilisation of ^{129}I (using ^{131}I as a surrogate) and ^{14}C. Performance tests (sorptivity, porosity and leaching tests) were used to determine waste-form durability. The results of this research indicate that the properties of the CBPC waste-forms when compared to the current cement matrix used at Vaalputs are superior. Excellent retention of iodine in the phosphate ceramic matrices was observed using the ANSI/ANS 16.1 leaching procedure tests, yielding an effective diffusivity rate as low as 10^{-15} cm^2s^{-1}. The excellent performance results of the newly created Zn-P ceramic as an anionic radionuclide immobilisation waste-form implies that this waste-form may also be considered for other "problematic" radionuclides such as ^{99}Tc, ^{14}C and ^{36}Cl

TABLE 12. SUMMARIZING OF RESULTS TO ENCAPSULATE DIFFERENT WASTE STREAMS

Waste Type	Composition of grout matrix used at Necsa
Graphite fuel spheres	CHEM 1 with Asphalt Additives
Sludge	CHEM 1 with Asphalt Additives
Resins	CHEM 1 with Asphalt Additives
Liquid	CHEM 1 with Asphalt or vermiculite as additive
Tritium	CHEM 1 with Asphalt Additives wit bitumen coating
Organics (oil/TBP)	CHEM 1, Nochar absorbent, Asphalt Additives, fibers.
Graphite dust	Cold ceramic as pre-cursor into CHEM 1 with Asphalt Additives
Tc and I waste	Cold ceramic as pre-cursor into CHEM 1 with Asphalt Additives

7. CONCLUSION

The durability of concrete is an important issue and the imaging thereof plays a major part in the understanding of the characteristics of concrete. As the attenuation of the concrete and water differs to a significant degree, the visualization of water in a concrete the sorptivity could be clearly visualized as the water front moves with time into the specimens. Porosity as well as sorptivity results obtained with NRad compared favorably with results from standard concrete tests.

To improve the characteristics of current grout/cement matrixes used for the encapsulation of radioactive waste, two different cement mixtures Cem 1 (96% OPC) and Cem 5 (mixture of 20% fly ash, 20% blast furnace slag and 60 % cement powder) were studied with the addition of different admixtures, inert fiber material and plasticisers. With no formal guidance from the WAC of the disposal site, it was decided that the following matrix requirements have to be met in order to qualify a possible matrix for radioactive waste immobilisation research:

- Total porosity less than 10 % (Implies a compression strength higher than 50 Mpa) and

- Sorptivity rate lower than 2.5 grams/hour (Implies pore structure not interlinked)

Results with radioactive waste indicated an admixture of bitumen or asphalt in CEM 1 (96% OPC cement) has the best characteristics and comply to the specified requirement.

The absorption of organics such as TBP and oil onto Nochar polymer systems have been demonstrated to be successful with no loss in activity. It has also been demonstrated that the polymer absorbed with organics (oil/tbp) can be encapsulated into cementitious grout. No leaching of radionuclides was observed and the tensile and compression strength of this matrix was improved with the addition of fibers.

REFERENCES

[1] KOZAK, M.W.,Vaalputs 2007 Post closure Radiological Safety Assessment: Evaluation of concrete drum performance, Report MSCI-2704-2 Revision 0.1, June 2007. (Monitor Scientific LLC Denver CO 80235 USA.

[2] ILLSTON, J.M., Domone, P.L.M., Construction Materials: their Nature and Behaviour (third ed.), Sponn Press, London (2001).

[3] KELHAM, M., A water absorption test for concrete, *Magazine Concrete Res.* **40** (1988) 143.

[4] DE BEER, F.C., Neutron radiography imaging, porosity and permeability in porous rocks, *South African Journal of Geology* **109** 4 (2006) 541.

[5] NEMEC, T., RANT, J., APIH, J., GLUMAC, V., *Nucl. Instr. and Meth. B* **424** (1999) 242.

[6] MIDDLETON, M.F., DE BEER, F.C., Corrections for quantitative neutron radiography, Proceedings of Seventh World Conference on Neutron Radiography.

[7] DE BEER, F.C., MIDDLETON, M.F., HILSON, J., Neutron radiography of porous rocks and iron ore, *Appl. Radiat. Isotopes* **61** (4) (2004) 487.

[8] BEYLEVELD, J. F., "Vaalputs Post-Closure Engineering Design", Internal Report VLP-SAC-06/003, South African Nuclear Energy Corporation, Pretoria (2006).

[9] MEYER, A.J., "Conditioning options for uranium contaminated Y-Plant oil", Necsa, GEA 1652 (2004).

[10] SORA, N. I., PELOSATO, R., BOTTA, D. DOTELLI, G.," Chemistry and Microstructure of Cement Pastes Admixed With Organic Liquids", *Journal of the European Ceramic Society* **22** (2002) 1463-1473.

[11] CAMPBELL, D., "Alara and cost savings success with highly contaminated liquid mixed waste solidification using NOCHAR® PETROBOND® polymer technology, EPRI/ISOE International ALARA Symposium (2005).

[12] Nochar Newsletter, Vol. 3, No. 1, February 2005.