ENCAPSULATION OF ILW RAFFINATE IN THE DOUNREAY CEMENTATION PLANT

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ABSTRACT

The Dounreay Cementation Plant has been designed and constraucted to encapsulate the first cycle liquid raffinate arising from the reprocessing of irradiated Reasearch Reactor fuel into a cementitious matrix. The acidic liquid waste is conditioned with sodium hydroxide prior to mixing with the cement powders (a 9:1 ratio of Blast Furnace Slag / Ordinary Portland Cement with 5% Lime). The complete cement mixing process is performed within the 500 litre drum which provides the waste package primary containment. The plant has recently been commissioned and has commenced routine operation, processing stocks of existing raffinate that has benn stored at Dounreay for up to 30 years. The waste loading per drum has been optimised within the constraints of the chemical composition of the raffinate, with an expected plant throughput of 2.5 m^3/week.

INTRODUCTION

The reprocessing of irradiated Research Reactor (RR) fuel has been performed on the Dounreay site since the early 1960's, with the first cycle raffinates being stored in large underground tanks (~70 m^3 capacity). The earliest raffinates have now been in storage for more than 30 years and by definition are classed as an Intermediate Level Waste (ILW) stream. It is UK Government policy to immobilise liquid ILW raffinates into a solid form at the earliest opportunity to reduce the overall risk to the workforce and public and minimise lifetime waste management costs. This has been implemented by the UKAEA for the above waste stream through a program of wasteform development culminating the construction and operation of the Dounreay Cementation Plant (DCP).

The DCP is a custom-built facility, specifically designed to incorporate the raffinate into a cementitious package, suitable for long-term storage and eventual disposal in a repository. The specific formulation has been determined following an extensive programme of development work resulting in a product which can be demonstrated to be 'essentially monolithic', with acceptable overall properties for the processing, storage, transport and disposal of these wastes. The plant design has been based upon a process to encapsulate the waste into a stainless steel 500 litre drum package, which complies with the current UK specification for long term disposal of ILW. The plant is currently programmed (over the next few years) to process the current stocks of RR raffinate held on site to facilitate eventual disposal to a national repository (when built). This work is performed such that the finished package meets with the anticipated criteria specified by Nirex, (and also overseas customers [3]) with an extensive quality assurance regime in place to fully demonstrate key product quality parameters.

PROCESS AND PLANT DESCRIPTION

The DCP has been specifically designed to condition and immobilise raffinate (1st cycle) arising from the reprocessing of RR fuel which is currently stored in large (~70 m^3) shielded stainless steel tanks. The contents of the tanks have been subjected to detailed analysis using quality assured techniques to provide an accurate account of the relevant radionuclide and chemical species. The raffinate as received in the DCP is acidic with a typical analysis as indicated in Table 1. The anion deficiency (AD) represents the degree of hydroxylation of the unneutralised liquor, ie $Al(NO_3)_{3-X}.(OH)_X$ which consists of a mixture of basic aluminium nitrates.

Aluminium (molar)	'Anion Deficiency' (molar)	Total Alpha (Bq/ml)	Total Beta (Bq/ml)	Total Gamma (Bq/ml)	Cs-137 (Bq/ml)	Uranium (g/l)	Plutonium (g/l)
2.0	0.85	1.9 E5	2.0E8	4.8E7	5.0E7	0.09	< 0.005

Table 1 Typical Analytical Data for Unconditioned MTR Raffinate

The liquor is transferred in batches (~2.5m^3) via a dedicated pipeline from the adjacent Raffinate Storage Plant to the DCP Reception Vessel (RV) where it is resampled for a 'finger-print' analysis to confirm it's acceptability for encapsulation and assess the optimum addition of sodium hydroxide for conditioning prior to cementation. The neutralisation is carried out by adding the acidic raffinate to concentrated sodium hydroxide ensuring that an excess is always present. During neutralisation, the acidic aluminium nitrate is converted to sodium aluminate which is soluble in the excess sodium hydroxide. The soluble sodium aluminate subsequently dissociates into sodium hydroxide and insoluble aluminium hydroxide thereby removing 'soluble' aluminium from the liquor. Development work has demonstrated that high soluble aluminium values could cause set retardation and large shrinkages adversely affecting product quality. It is therefore essential that the neutralised solution is allowed to approach equilibrium prior to commencing encapsulation.

The specific cement powder formulation was evolved from an extensive programme of development work since the 1980's. The objectives were to identify a formulation which would give a satisfactory cementitious wasteform suitable for long term storage and disposal. Early work [1] confirmed that the preferred matrix materials for incorporating nitrate based wastes was a mixture of Blast Furnace Slag (BFS) and Ordinary Portland Cement (OPC) with a weight ratio of 9:1. The optimum waste/cement loading was also identified to be around 0.55 w/c. Later work [2] indicated that improved wasteform dimensional stability characteristics could be obtained by adding 5% lime ($Ca(OH_2)$) to the cement powder formulation. A wide range of product quality characteristics were checked and verified during the development programme including compressive strength, permeability, gas generation, dimensional stability, radiation stability, density, and heat output. The majority of these are relatively constant regardless of relatively minor variations in the waste and/or cement powder constituents, and it is perhaps the dimensional stability characteristic that is the most crucial in determining good long-term performance of wasteform. One of the key features is obtaining an 'essentially monolithic' block which will retain it's overall shape and still be handleable even if the drum is removed. The degree of cracking is a function of the product shrinkage during the cement curing process with experimental work indicating that shrinkages of less than 2500 microstrain after 90 days curing would result in an acceptable product. Tests on the formulation of BFS/OPC/lime used in the process have confirmed that the shrinkage is less than 2000 microstrain with rate of dimensional changes decreasing with time. Drums produced during inactive trials have also been sectioned and the outer drum removed to demonstrate that the degree of cracking is acceptable.

The drum itself is manufactured from 316S11 stainless steel and conforms to the specifications laid down by Nirex for long term storage and disposal of ILW in an underground repository, and is very similar to drums produced by BNFL for their comparable wastes. A schematic drawing of the drum in section is shown in Figure 1. It has overall dimensions of 800 mm diameter by 1190 mm high, with a drum body wall thickness of 2.5 mm and incorporates a 'standard' annular lifting feature in the lid flange of the drum. It also includes a captive mild steel paddle used to perform the cement mixing process within the drum and is vented through a sintered stainless steel filter (rated to 0.3

micron) to prevent any possibility of drum failure due to gas pressurisation. It is worth noting however that the potential for significant gas evolution (due to corrosion or radiolytical degradation, etc) from the wasteform is negligible. The package has been assessed for the effects of both internal and external corrosion, impact performance, and stability under storage conditions. These have all concluded that there are no features which would render the drum unhandleable after at least 50 years. Since the heat output from the drums due to radiolytical decay will be typically less than 3 W/drum there is no requirement to provide any cooling during either storage or future transport.

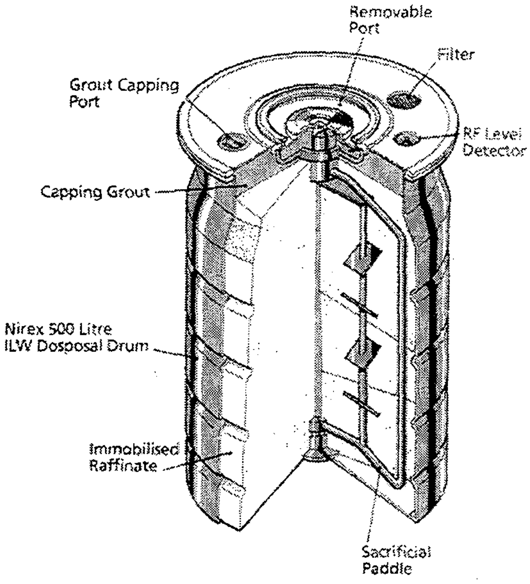

Figure 1 - DCP 500 litre Drum

The layout of the plant is shown schematically in Figures 2. Essentially the plant may be divided into three main areas, the chemical cell, the main handling cell (MHC), and the interim drum store (IDS), supported by the ancillary equipment and services. The receipt and conditioning of the raffinate is all performed within the chemical cell which houses the three main liquor vessels, ie the Reception, Mixing, and Washings Vessels with nominal volumes of 3.9 m^3, 5.8 m^3, and 3.9 m^3 respectively. The liquor transfer operations are all performed using fluidic pumps, with force lift steam ejectors provided as backup. The conditioning/neutralisation process is carried out in the Mixing Vessel: wher a predetermined quantity of sodium hydroxide is added to the vessel followed by the appropriate volume of raffinate. The vessel is continuously stirred to ensure that the precipitate formed is maintained in suspension and that the solution fed to the drums for cementation remains homogeneous. Once the conditioned liquor is ready for encapsulating, it is pumped up to the Transfer Pot vessel which is fitted with an overflow return line that has been set to give a constant volume of exactly 266 litres. This fixed volume is then drained by gravity directly into the drum already located at the Mixing Station in the MHC.

The drum is mated with a double-lidded port on the underside of the Mixing Station which is essentially a glovebox to provide containment and minimise the potential spread of contamination. All other areas within the shielded area of the MHC are thereby kept clean, significantly simplifying access to the cell when required (maintenance etc). The cement powders for each drum are weighed, mixed and transferred across to the Cement Hopper. They are then fed into the drum at a controlled rate as the drum is stirred via the captive in-drum paddle: the complete mixing process taking approximately 2 hours per drum. The active grout is allowed to stand for a minimum of 24 hours to ensure curing is complete before transfer along the MHC conveyor to the inspection and inactive grout cap stations. The void between the active grout and the underside of the drum lid is filled by topping up the drum with an inactive grout (3:1 Pulverised Fly Ash (PFA) : OPC). The external surfaces of the drum are swabbed to check for any surface contamination before transfer to the contiguous drum store. A drum decontamination facility is available should any drums require cleaning. A schematic diagramm of the DCP process is shown in Figure 3.

The interim drum store is of a vault design with the free-standing drums stacked up to 5 high and has capacity to hold 1200 drums (ie ~30 % of the current raffinate stocks). A drum store extension is currently under construction to accommodate the drums from the remaining volume of raffinate.

Provision has also been made for the installation of a drum export facility which is currently at the conceptual design stage. This will facilitate the transport of cemented drums to a national repository or other customers as appropriate.

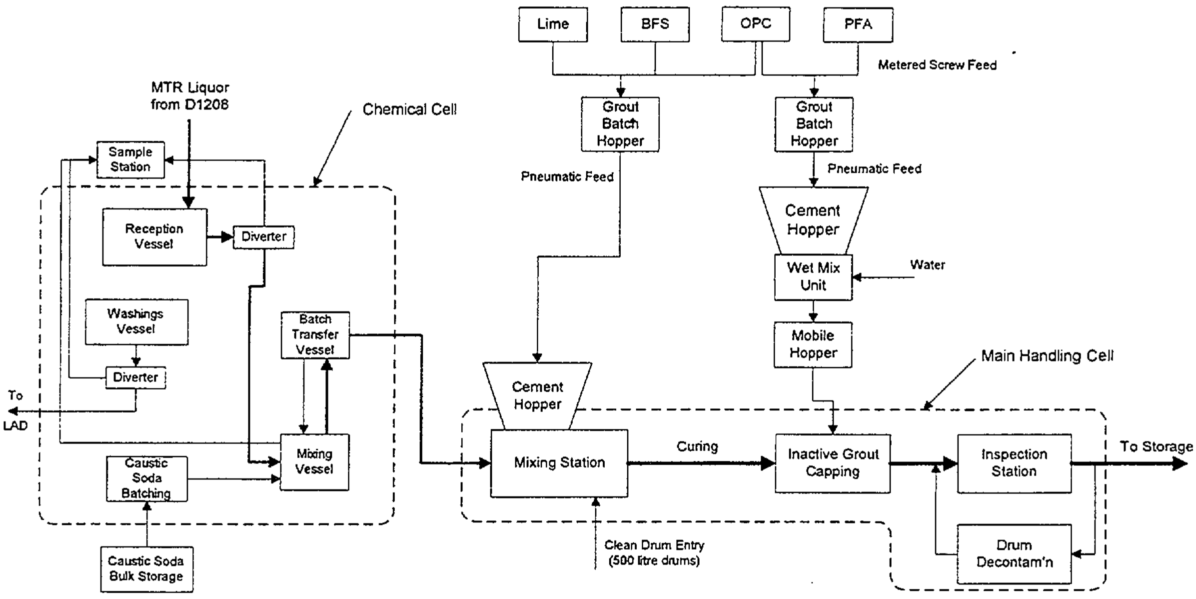

Figure 3 - Schematic Diagram of the DCP Cementation Process

OPERATIONAL EXPERIENCE

The plant was built and virtually ready to commence operations in the late 1980's when Nirex announced that it's standard drum package would be a 500 litre capacity stainless steel drum, rather than the 200 litre drum that the plant had been designed to produce. Consequently UKAEA decided to modify the plant to accommodate this key change and also take cognisance of other changes to the Dounreay site strategy for managing it's solid ILW streams. The cementation process aspects were modified and commissioned inactively during 1995. Consent to commence active commissioning was obtained from the regulators in late 1996 which culminated in a total of 120 drums being successfully processed through the plant. Regulatory consent to continue with full routine operation of the plant is expected in early 1998, to continue the programme of raffinate encapsulation for the next 7-10 years. Some of the key features of plant commissioning and operation to date are discussed below.

The inactive commissioning trials successfully demonstrated that the plant's operational envelope was well within the acceptable range of formulation variations which would still produce a fully satisfactory product. Only major process or plant failures, which would be noticed and corrected, would result in potentially out of specification product. A random selection of the drums produced during inactive commissioning were sectioned to confirm the homogenuity of the in-drum mixing and that the degree of cracking was acceptable, resulting in an essentially monolithic block. The destructive analysis also confirmed that parameters such as density, compressive strength, and voidage were all well within acceptance criteria.

Some minor contamination of the drum lid (localised to the filling port seal) was experienced during active commissioning: this has been addressed by improving the port design and dust disentrainmnet systems. The general radiation levels from the cemented drums have been measured at ~800 mSv/hr γ, comparing very favourably with the predicted value of 900 mSv/hr. The analysis of raffinate samples taken upon receipt of the liquor in the DCP have shown a high degree of consistency lending further confidence to the excellent homogenuity of the final encapsulated waste product.

The opportunity to further optimise the process was taken during the commissioning. The process flowsheet identified from the development work required the addition of up to 5 % excess sodium hydroxide to ensure that the conditioned liquor was always alkaline. However confidence in the operability of the plant allowed this excess to be removed thereby increasing the waste loading in the final cemented product. Ultimately however the waste loading is dependent upon the aluminium concentration and acidity of the raffinate to be conditioned.

The plant's ability to meet it's design throughput of 2.5 m^3 of raffinate per week, ie equivalent to ~14 drums/week, has been successfully demonstrated in the operations to date. The overall throughput is also being further optimised by reviewing the individual unit processes to identify opportunities for improvements.

Since the product waste drums will eventually be consigned to either a UK national repository or returned to overseas commercial customers as appropriate [3], it is vital that the key product quality parameters are recorded and documented in a fully auditable manner. Consequently the DCP process is covered by a fully developed record system in compliance with specific customer needs. The UKAEA at Dounreay is certificated to BS EN ISO 9001:1994 and BS5882:1996, with the plant quality assurance management system meeting these requirements.

REFERENCES

[1] C G Howard & D J Lee, Immobilisation of MTR Waste in Cement (Product Evluation), January 1988, AEEW-R 2312.

[2] T R Holland, C G Howard & D J Lee, Immobilisation of MTR Waste in Cement wsate form Reformulation Studies, April 1992, AEA-D&R-0344.

[3] Intermediate Level Residue Specification, Dounreay Cemented Liquid Wastes, February 1992.

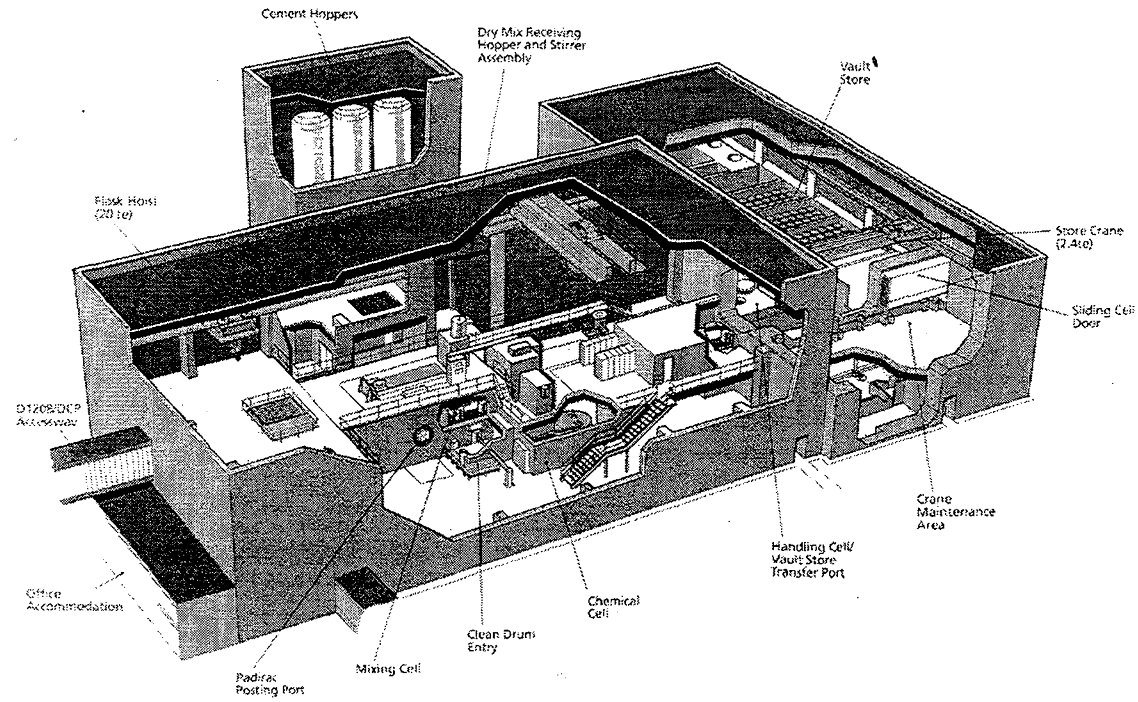

Figure 2 - Schematic Diagram of the Dounreay Cementation Plant