The Crystallisation of Irradiated MOX Fuel

Document Prepared by Other Institute, Based on the Contract

February, 2002

SUMMIT AEA CORPORATION

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(Document on Present State of Affair)

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Two crystallisation tests have been carried out with irradiated MOX fuel solution. In the first test, MOX1, the final temperature of the solution was 10°C. In the second test, MOX 2, the final temperature of the solution was 0°C. The conclusions of the tests were as follows.

1. Spontaneous crystallisation of uranyl nitrate hexahydrate (UNH) occurred in both tests at approximately 28°C. This is less than the 32°C observed with pure uranyl nitrate/nitric acid solutions, possibly because of the presence of fission product impurities and plutonium (Pu).

2. The MOX 2 test gave, as expected, a higher yield of UNH crystals than the MOX 1 test. The U hold-up ratio (U in crystals as a proportion of the total U in the MOX feed to the process) was 0.57 and 0.68 for MOX 1 and MOX 2 respectively.

3. The hold-up of Pu in the UNH crystals (Pu in crystals by direct analysis as a proportion of the total Pu in the MOX feed to the process) was very low, with values for the final crystals after three scrubs of 8.2E-04 for MOX 1 and 1.03E-03 for MOX 2.

4. The U concentration in the damp crystals was very similar for both MOX 1 and MOX 2, at 0.488g/g and 0.484g/g respectively, which is within 2% - 3% of the theoretical stochiometric ratio for pure UNH.

5. The good agreement of the U concentration in the crystals with that for pure UNH indicates that very little liquid was held up in the crystals after filtration. However, the quantity of actinide and fission product impurities scrubbed from the UNH crystals was relatively high, in terms of volumes and concentrations of the filtrate solutions. Therefore scrubbing possibly leached the actinides and fission products from the UNH crystals, rather than diluted and removed liquid held up in the crystals.

6. High decontamination of the UNH crystals from Pu and the main actinide and fission product impurities was achieved by scrubbing. For example, DFs for [241]Am, [244]Cm, [134/137]Cs and [154/155]Eu were generally about 700 to 900 for MOX 1 and 1200 to 2500 for MOX 2. The DFs for Pu in the final crystals were similar for both MOX 1 and MOX 2, at just under 700. For MOX 2, the significantly lower DF for Pu than for the other actinides and fission products (except [125]Sb) might indicate that the mechanism of Pu hold-up in the crystals differs from that of the other radionuclide impurities.

7. The DFs for MOX 2 were lower for the initial crystals than for MOX 1 but were higher for the final crystals after three scrubs. The data on the volume and estimated weight of the crystal beds indicates that the density of the MOX 2 crystal bed was somewhat lower than for MOX 1. Hence, the MOX 2 crystals might have had a more open structure which resulted in an initial higher hold-up of impurities but more efficient leaching during the scrub process.

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MOX   2   MOX
10   2   MOX   0

UNH   28
32   Pu   FP

MOX   MOX   UNH   U
MOX   U   U   0.57   0.68

UNH   Pu   MOX   Pu
      Pu   MOX
8.2E-04   MOX   1.03E-03

            U   MOX   0.488g/g
0.484g/g   UNH   2% - 3%

      U   UNH   U   MOX
                                                      UNH

      FP

                              FP   UNH

Pu   UNH   FP
      ^{241}Am, ^{244}Cm, $^{134/137}$Cs $^{154/155}$Eu   MOX   700   900 MOX
            1200   2500   Pu
   MOX   700   MOX   Pu
^{125}Sb   FP   Pu

MOX   MOX   3
                                                      MOX
   MOX   MOX

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Appendices

1 Introduction

The separation and purification of uranium from reprocessing streams by crystallisation offers many advantages over the current solvent extraction process[1]. Some potential advantages are as follows:

- the relative simplicity for remote operation[1,2]
- the removal of an organic phase and consequent fire hazard[2]
- the expected reduction of the reaction vessel size requiring smaller active facilities[1,2]
- reduced waste volumes and consequently reduced costs[1,2]

In order to prove the viability of this process confirmation is required that the uranyl hexahydrate (UNH) crystals do not contain crystallised Pu since this would complicate the treatment of the UNH crystals at a later stage in the process. Therefore a series of experiments have been performed to provide specific data on the crystallisation temperature of Pu in selected solutions, which are not currently available in public literature.

The first stage of work investigated the crystallisation of Pu(IV) solutions containing 50, 100 and 200 g/l Pu(IV) in 4 and 6M HNO_3. The results[3] indicated that Pu(IV) did not crystallise, rather the associated HNO_3 and water did crystallise.

During stage 2 of this programme of work the crystallisation of Pu(VI) and mixed U(VI)/Pu(VI) solutions were investigated. The results[4] showed that Pu(VI) alone did not crystallise but in the mixed system co-crystallisation occurred resulting in crystals containing approximately the same U:Pu ratio as in the starting solution. This result was not surprising due to the chemical similarities of U(VI) and Pu(VI)

This report gives the results of two crystallisation experiments performed on mixed U(VI)/Pu(IV) solutions. The solutions were prepared by dissolution of irradiated MOX fuel that contained approximately 10% Pu. Due to the highly radioactive nature of this material the experiments were performed in a hot-cell.

2 Experimental method

2.1 PREPARATION OF SOLUTIONS

The initial MOX fuel solution was prepared by dissolution of MOX fuel in Zircaloy cladding. Several fuel pins were cut into about 25mm lengths using a pipe cutter and loaded into a stainless steel basket. The stainless steel basket was then lowered into a dissolution vessel containing 9.5M HNO_3. The lid of the vessel was clamped into place and the solution heated to ~100°C by means of an electrical band heater. During dissolution, the NOx fumes produced passed through a condenser attached to the lid and then through an engineered scrubber.

The dissolution was allowed to proceed for 8 hours and then the heater turned off. Once the solution had cooled it was pumped to an interim storage bottle and then filtered under vacuum through a 0.45μm microfilter.

A total of three dissolutions were performed and the resulting product diluted with nitric acid to produce about 3.2 litres of solution. The solution was analysed by UV/vis spectrophotometry for U and Pu, and also by titration for acidity, and found to contain $237 \pm 12gU/l$ and $24 \pm 2gPu/l$, and $4.7 \pm 0.2M$ HNO_3. The product solution and undissolved residues are shown in Photographs 1 and 2 in Appendix 2.

Approximately 500ml of the MOX solution were then taken for further processing to produce a solution suitable for the crystallisation tests. The remainder of the MOX solution was stored for an extraction experiment.

The 500ml of solution taken for the crystallisation experiments was placed in a glass vessel and distilled in order to raise the heavy metal content (U + Pu) of the solution. When the volume of the solution had reduced to 250ml, distillation was stopped and the solution analysed. The acidity of the solution was much higher than required and therefore it was necessary to continue the distillation and then add water. This process effectively drove off the excess acid and a final solution containing $456 \pm 23gU/l$ and $47 \pm 3g/l$ Pu in $4.6M \pm 0.2M$ HNO_3 was produced.

The UV/vis spectrophotometry measurements on the intermediate solution, at the 250mls stage, indicated that Pu(IV) was oxidised during distillation almost completely to Pu(VI). It was therefore necessary to adjust the Pu back to the tetravalent state by careful addition of a stoichiometric amount of H_2O_2. (Alternatively, NOX was considered but the gas could not be obtained on an acceptable timescale. Sodium nitrite was also considered but rejected because this would result in the addition of sodium ions). The solution was kept warm during addition of the hydrogen peroxide, to ensure all the U and Pu remained in solution. Analysis indicated that this process had worked well and the feed solution contained only tetravalent Pu. There was no evidence of any insoluble precipitates during or after the addition of hydrogen peroxide.

The concentrations of U and Pu and the acidity of the final solution was confirmed again and two 100ml portions separated into storage vessels. The vessels had been pre-calibrated with Vernier scales to enable the volume of MOX solution to be accurately determined. The residual solution was saved for later use if required.

Scrub solutions were prepared by dissolution of the required quantity of uranyl nitrate hexahydrate (UNH) in distilled water. Concentrated HNO_3 was added to produce the required acidity. Two sets of scrub solutions were prepared. The first set contained approximately 200g/l U in 5M HNO_3 and was used for the first experiment that had a final temperature of $10^{o}C$. The second set contained approximately 150g/l U in 5M HNO_3 and was used for the second experiment where the solution was cooled to $0^{o}C$.

2.2 CRYSTALLISATION EQUIPMENT

A schematic diagram of the crystallisation equipment used for this work is shown in Figure 1. It is similar in design to that used during the previous U(VI)/Pu(VI) experiments[4] although the configuration has been modified to facilitate remote handling techniques in the hot-cell.

The equipment consisted of three vessels, a crystallisation vessel, a scrub/filtration vessel and a scrub feed vessel. Each of these vessels had a jacket containing a recirculated thermo-regulation fluid so that the vessel and contents could be heated or cooled to the required temperature. Heating or cooling was achieved using a Huber Unistat 385 unit that used silicone oil as the thermo-regulation fluid. The Huber Unistat had a working range of $+60^{o}C$ to $-60^{o}C$ and was driven by proprietary software on a PC that allowed the rate of cooling/heating and final steady-state temperature to be controlled automatically.

The crystallisation vessel contained a mechanical stirrer to ensure good mixing and a platinum resistance thermometer (PRT). The PRT was connected to the Unistat system so that the solution temperature could be recorded during the experiments and displayed, together with the coolant temperature and control set-point temperature, on the PC screen.

The scrub/filtration vessel was fitted with a glass frit so that the crystals could be filtered. A sample bottle was connected to the glass outlet tube of the filtration vessel, by a plastic bung, to collect the filtrate. A plastic tube through the bung was connected to a vacuum pump, by a 'quick-release' ball and socket joint, to enable vacuum suction of the filtrate.

The scrub feed vessel was used to cool the scrub solutions to the final steady-state temperature, so that the scrub solution would not dissolve a significant mass of crystals when added to the scrub/filtration vessel. For the first MOX test, the temperature of the scrub vessel was monitored by means of a thermocouple and in-cell digital recorder. For the second MOX test, the scrub vessel temperature was monitored by the PRT. (After its use in the crystallisation vessel, the PRT was cleaned three times with water and nitric acid before use in the scrub vessel).

The equipment is shown set up in the hot cell in Photograph 3.

The PRT and thermocouple were calibrated by immersing them in pure water, which was first heated to the boiling point and then cooled to the freezing point. The PRT indicated $99.9^{o}C$ at the boiling point and $0.1^{o}C$ at the freezing point. The thermocouple was less accurate, possibly because the in-cell display had deteriorated due to irradiation. Therefore, a correction factor was applied to the thermocouple measurement when it was used to check the scrub acid feed temperature in MOX test 1. (At $0^{o}C$ the thermocouple display was unreliable and hence the PRT was used to check scrub acid temperature).

2.3 EXPERIMENTAL PROCEDURE

2.3.1 U commissioning test

Although two uranium trials had been carried out in the laboratory, a commissioning test in the hot cell was necessary to ensure:

a) the Unistat heating and cooling programme was adequate for the slightly different arrangements which applied in the hot cell (for example, longer cooling lines)

b) all the stages of the process could be operated smoothly and samples taken as planned with the telemanipulators

c) the measured crystallisation temperature agreed with previous measurements of the uranyl nitrate/nitric acid system.

Approximately 100mls of a solution of 500gU/l in 5M nitric acid was therefore put through the test procedure described in the next Section for the MOX test 1, up to and including the first scrub.

2.3.2   MOX test 1

One of the portions of feed solution was gently warmed on a hotplate to 40°C to dissolve the crystals that had clearly formed during the brief period of storage at ambient temperature. At the same time the Unistat heat-exchange unit was started and set to 40°C. When all the crystals had redissolved the solution was transferred to the crystallisation vessel and the stirrer started. At the same time 50ml of scrub solution (approximately 200gU/l in 5M HNO_3) was place in the scrub vessel. The temperature was allowed to stabilise at 40°C.

The Unistat unit was programmed to reduce the coolant temperature to 2°C at approximately -0.5^{o}C/min. The commissioning test with the U solution had indicated that, at this final set-point temperature, the fuel solution would cool to the required temperature of 10°C. The difference in temperatures between the coolant and MOX solution is due to warming of the coolant in the tubes that feed the coolant from outside the hot-cell to the crystallisation vessels.

When considering the test procedure, it was envisaged that, when the temperature of the solution reached 32°C, a uranyl nitrate hexahydrate (UNH) crystal weighing ~0.05g would be added to act as a seed for crystallisation. However, crystals were evident in the MOX solution before it was warmed for the test and therefore it was decided that seeding was unnecessary. As cooling continued below 32°C, and more crystals formed, the stirring speed was increased gradually to ensure good mixing.

When the temperature of the solution reached 10°C it was maintained for at least 5 minutes. The temperature inside the scrub/filtration vessel was checked with the thermocouple system and then, while still stirring, valve V1 was opened to allow the crystals to transfer to the scrub/filtration vessel. Valve V2 was opened to allow liquid to drain to the sample bottle underneath and vacuum was applied so that the residual solution was sucked through into the collection bottle. Vacuum aspiration was maintained for at least 3 minutes. After the allotted time, vacuum filtration was stopped, valve V2 was closed, and the collection bottle was removed and replaced with a clean one (for the first scrub liquid). The volume of crystals in the scrub/filtration vessel was estimated by means of the Vernier scale attached to the side of the vessel and then a small sample of crystals (~0.5g) taken for analysis.

The crystallisation vessel was moved out of the way of the filtration vessel. The temperature of the scrub solution was confirmed as 10°C with the thermocouple and in-cell display, and valve V3 opened. When all the scrub solution had drained into the scrub/filtration vessel,

valve V3 was closed and the crystals and scrub solution gently mixed using the stirrer from the crystallisation vessel for at least 1 minute. After stirring, valve V2 was opened, the stirrer removed from the slurry, and vacuum applied to suck the solution into the second collection vessel. Vacuum aspiration again lasted for at least 3 minutes and then V2 was closed.

Another 50ml portion of scrub solution was measured into the scrub vessel and allowed to cool to 10°C. While awaiting for the scrub solution to reach temperature the volume of crystals in the scrub/filtration vessel was estimated and then a small sample taken for analysis. The liquid collection bottle was replaced with a clean one.

The above scrubbing process was repeated until a total of three scrubs had been performed. After each scrub the crystal volume was estimated and a small sample taken for analysis.

The volume of solution in each of the scrub collection vessels was determined with a measuring cylinder and the solution stored for later analysis.

2.3.3   MOX test 2

The second crystallisation test, using the other 100ml portion of feed solution, was performed in the same way as described above with the following differences.

1)   The final temperature of the MOX solution was 0°C. To achieve this, the Unistat unit was programmed to reduce the coolant temperature to -5°C at approximately -0.5°C/min.
2)   The scrub solution contained approximately 150g/l U in 5M HNO_3
3)   The PRT was used to measure the scrub acid temperature, since the thermocouple system had been found to be unreliable at this temperature.

2.4   CALCULATION OF MASS OF CRYSTALS, HOLD-UP RATIOS AND DF

2.4.1   Mass of crystals

The following mass balances are applied to the results in Section 4.

U in crystals = U in initial MOX feed solution – U in L-0 'mother' liquor   (1)

(Such a mass balance could also be applied to the scrubbed crystals provided there is a significant difference between the U concentration in the scrub feed and scrub filtrate. However, it will be seen that there were not any significant differences of U concentration in the scrub solutions).

The U concentration in the damp crystals (gU/g of damp crystals) was determined by analysis of a known weight of crystals dissolved in a known volume of solution, as described in Section 3. Hence, the proportion of elemental U in the damp crystals can be compared with a value of 0.474 for pure uranyl nitrate hexahydrate (UNH). These data can also be used to calculate the total mass of damp crystals as follows.

Total mass of damp crystals = $\dfrac{\text{mass of U in crystals (from equation (1)}}{\text{U concentration in crystals (gU/g)}}$ (2)

The density of the crystal bed may be calculated by dividing the total mass of damp crystals by the volume of crystals.

2.4.2   Hold-up Ratios

U hold-up ratio = $\dfrac{\text{U in crystals}}{\text{U in initial MOX feed solution}}$ (3)

where the mass of U in the crystals is calculated from equation (1).

The Pu hold-up ratio for the crystals at each stage of scrubbing can be calculated in the same way as the U hold-up ratio, from the following equation:

Pu hold-up ratio = $\dfrac{\text{Pu in initial MOX feed solution – total Pu in filtrate solutions}}{\text{Pu in initial MOX feed solution}}$ (4)

The disadvantage of equation (4) is that the good separation performance of U and Pu resulted in a high concentration of Pu in the initial 'mother' liquor and therefore a considerable error in subtracting the total Pu in the filtrate solutions from the Pu in initial MOX solution.

Alternatively, the Pu hold-up ratio may be calculated as:

Pu hold-up ratio = $\dfrac{\text{Pu in crystals by direct analysis of the crystals}}{\text{Pu in initial MOX feed solution}}$ (5)

2.4.3   DFs

All DFs are calculated with respect to the mass of U.

The DF for Pu, at each stage of the process, is calculated from the masses of Pu, i.e.

DF for Pu = $\dfrac{\text{Mass of Pu/g U in the MOX feed solution}}{\text{Mass of Pu/g U in crystals}}$ (6)

The DFs for the measured fission products, ^{241}Am and ^{244}Cm, are calculated from the radioactivity of these species, i.e.

DF = $\dfrac{\text{Bq/g U in the MOX feed solution}}{\text{Bq /g U in crystals}}$ (7)

3   Analysis

The following analytical techniques were applied to the samples.

a) U in concentrations above 0.5g/l and Pu in concentrations above 0.05g/l, and Pu valence, were measured by UV/visible spectrophotometry. This technique required a 0.1ml aliquot of process solution to be taken with a pre-calibrated Gilsen® pipette, and diluted with 3mls or 5mls of 6M nitric acid to be within the range of the instrument. The nitric acid was dispensed from a stock solution with a 1ml capacity Gilsen® pipette. The overall precision of this technique is ±5% for the concentrations measured, including dilution errors.

Crystals were prepared for analysis by weighing a portion of the sample of the crystals and dissolving the portion in 6M nitric acid. The quantity of nitric acid (generally about 5mls) was calculated so that the product solution would be within the optimal range of the spectrophotometer. The product solution was therefore added directly to the spectrophotometer cuvette, without the need for any further dilutions. The product solution was weighed and the volume of solution calculated from the density of the acid, which had been measured beforehand.

b) Nitric acid concentration was determined by titrating a sample of solution, buffered with potassium fluoride to complex U and Pu, with 0.1M sodium hydroxide solution using phenolphthalein indicator. The 1ml capacity Gilsen® pipette was used to dispense the initial quantities of sodium hydroxide solution and the 0.1ml capacity Gilsen® pipette to dispense the quantities when close to the end point. The overall precision of the technique is ±0.2M.

c) Pu in concentrations below about 0.05g/l was analysed by alpha spectrometry. An aliquot of the solution prepared for UV/visible spectrophotometry was further diluted so that it could be safely posted from the hot cell into a fume cupboard, for preparation of a dried film for alpha counting. The 0.1mm Gilsen® pipette and calibrated volumetric flasks were used for this purpose. The total Pu in the sample was calculated from the ^{239}Pu/^{240}Pu detected by alpha counting, and the isotopic composition of the Pu which had been measured previously by mass spectrometry (1.596wt% ^{238}Pu, 54.584wt% ^{239}Pu, 32.456wt% ^{240}Pu, 5.241wt% ^{241}Pu, 6.123wt% ^{242}Pu).

d) The main fission products, ^{134}Cs, ^{137}Cs, ^{154}Eu, ^{155}Eu and ^{241}Am were detected by gamma spectrometry. The solution was diluted and prepared for counting as described in c) above. It was not possible to detect ^{144}Ce or ^{106}Ru by this technique, as they had decayed due to their relatively short half-life and because the main fission products interfered with their gamma emissions. The limits of detection for ^{144}Ce and ^{106}Ru were approximately 1E08Bq/ml and 5E08Bq/ml respectively for concentrated solutions (MOX feed and L-0 'mother' liquors) and both about 2E05Bq/ml for product crystals and dilute solutions (L-3 final scrub solutions). However, it was possible to detect ^{125}Sb, although interference by other gamma emissions resulted in a higher ± error on the measurements than was the case for the main fission products and ^{241}Am.

e) Samples of solution were analysed for ^{244}Cm by alpha spectrometry. A sample of the final dissolved crystals were deposited directly onto a plate and then counted.

4   Results

4.1   U COMMISSIONING TEST

As Figure 2 shows, the uranyl nitrate started to crystallise at just below 32^oC and an exotherm was clearly evident from a rise in solution temperature by 1^oC - 2^oC over the following minute. (Please note that the apparent steep drop in temperature at about 100 minutes was due to the cooling system being switched off for a short time. This did not affect the temperature of the crystallisation vessel).

Approximately 50mls of crystals were produced which appeared very pale under the lighting conditions in the hot cell.

4.2   MOX TEST 1

4.2.1   Crystallisation behaviour

The MOX solution was a very dark green colour, under the lighting conditions in the hot cell, as shown in Photograph 4.

The MOX solution started to crystallise at between 28^oC and 29^oC. This is seen in Figure 3 as an arrest in the rate of decrease of solution temperature, rather than a distinct rise in temperature, as observed for the U commissioning test. This is possibly because the rate of decrease in solution temperature was actually somewhat higher, and closer to the target, for the MOX test compared with the U commissioning test (between about $–0.5^oC$ and $–0.6^oC$, and between about $–0.3^oC$ and $–0.4^oC$ respectively).

As the temperature decreased further, crystals were clearly evident and towards the steady-state set point of 10^oC the solution had become less intensely dark green. The filtered crystals (1 C-0) were light green in colour, as shown in Photograph 5. After the three scrubs, the crystals were a very pale colour, as Photograph 6 shows, and had a similar appearance to the pure UNH crystals produced in the U commissioning test.

4.2.2   Volumes and chemical compositions of crystals and solutions

The measured volumes of the crystals and solutions are given in Table 1 below. The precision of the volume measurements is ±0.5mls and ±2.5mls for the liquids and crystals respectively. The concentrations of U, Pu and nitric acid are also given in Table 1. The U and Pu concentrations in the crystals are given as mg/g of damp crystal.

The collected solutions and samples of crystals are shown in Photograph 7.

Table 1. Concentrations of U, Pu and nitric acid for MOX test 1, (cooled to 10°C).

Sample		Volume (mls)	U conc.	Pu conc.	Pu valence	HNO$_3$ (M)
MOX feed solution before crystallisation		97	456mg/ml	47.4mg/ml	(IV)	4.6
Scrub solution	1	50	208mg/ml	-	-	5.5
	2	49	208mg/ml	-	-	5.5
	3	51	208mg/ml	-	-	5.5
Crystals	C-0	43	507mg/g	3.66mg/g	-	-
	C-1	28	476mg/g	3.93E-01mg/g	-	-
	C-2	28	509mg/g	2.06E-01mg/g	-	-
	C-3	30	480mg/g	7.32E-02mg/g	-	-
Solution after crystallisation	L-0	64	297mg/ml	68.2mg/ml	(IV)	6.6
Scrub solutions after washing	L-1	50	203mg/ml	7.7mg/ml	-	5.9
	L-2	48	203mg/ml	0.6mg/ml	-	5.7
	L-3	51	206mg/ml	5.83E-02mg/ml	-	5.4

The data in Table 1 show the following features.

- The average U concentration in the scrubbed crystals (C-1 to C-3 inclusive) is 0.488g/g which is 2% above the theoretical stoichiometric quantity of 0.474g/g for pure UNH. It is clear from this close agreement between the actual and stoichiometric concentration of U in the crystals that the mass of liquid held up in the crystals must be very small. However, the concentration of Pu in the scrub filtrates would correspond to a significant hold-up of liquid from the previous step. (For example, the Pu in the first scrub filtrate, L-1, is equivalent to between 5mls and 6mls of the L-0 'mother' liquor). This discrepancy possibly indicates that scrubbing leached Pu from the crystal matrix, rather than diluted held-up liquid. The same observation applies to the [241]Am and fission product data below.

- The volume of scrubbed crystals was between 28mls and 30mls. The initial volume of 43mls is higher than these values because the surface of the crystal bed was uneven and therefore the error in the measurement was high. (Also, there is no evidence of an increase in U concentration in the scrub solutions due to dissolution of crystals).

- Pu concentration in the crystals was low and decreased with each scrub. The very low Pu concentration in the final crystals is consistent with the observation that the final crystals were very pale in colour and similar to those produced in the U commissioning test.

- UV-visible spectrophotometry confirmed that all the Pu (within the limit of detection corresponding to about 0.1% of the total Pu) in both the MOX feed solution and the L-0 'mother' liquor was present as Pu(IV). The UV-visible spectra for the MOX feed and L-0 'mother' liquor are shown in Figures 4 and 5 respectively and there is no evidence of a peak at the wavelength of 830nm associated with Pu(VI).

The concentrations of the main elements, not including [244]Cm, are given in Table 2 below.

Table 2. Concentrations of main elements determined by gamma spectrometry[*] for MOX test 1, (cooled to 10°C).

Sample		Concentrations in Bq/ml for solutions and Bq/g for crystals					
		^{241}Am	^{134}Cs	^{137}Cs	^{154}Eu	^{155}Eu	^{125}Sb
Feed solution before crystallisation		1.96E08	1.92E06	5.47E08	6.02E06	4.81E06	1.63E06
Crystals	C-0	1.75E07	1.78E05	4.80E07	5.58E05	4.65E05	1.18E05
	C-1	1.99E06	3.27E04	5.65E06	6.31E04	5.09E04	6.41E04
	C-2	8.92E05	1.35E04	3.56E06	2.80E04	2.20E04	9.63E03
	C-3	2.49E05	3.03E03	7.75E05	6.99E03	5.85E03	4.10E03
Solution after crystallisation	L-0	2.92E08	2.86E06	7.92E08	9.22E06	7.80E06	1.92E06
Scrub solutions after washing	L-1	3.04E07	3.08E05	8.28E07	9.58E05	7.50E05	1.41E05
	L-2	2.54E06	2.71E04	6.96E06	8.02E04	6.31E04	2.34E04
	L-3	2.24E05	3.90E03	7.67E05	7.27E03	6.23E03	5.18E03

*Note: precision of analysis is generally approximately between ±1% and ±3% except for ^{125}Sb, which was ±5% for the L-3 scrub sample and between ±11% and ±24% for the other samples because of interference by other gamma emissions.

The concentrations of $^{239/240}$Pu and ^{244}Cm, determined by alpha spectrometry, are given in Table 3 below.

Table 3. Concentrations of plutonium isotopes and curium determined by alpha spectrometry for MOX test 1, (cooled to 10°C).

Sample		Concentrations in Bq/ml for solutions and Bq/g for crystals		
		$^{239/240}$Pu[(1)]	Total Pu[(2)]	^{244}Cm[(3)]
Feed solution before crystallisation		-	-[(4)]	1.83E07
Crystals	C-0	7.32E06	3.66mg/g	-
	C-1	7.87E05	3.93E-01mg/g	-
	C-2	4.12E05	2.06E-01mg/g	-
	C-3	1.46E05	7.32E-02mg/g	2.17E04
Scrub solutions after washing	L-1	-	-[(4)]	-
	L-2	-	-[(4)]	-
	L-3	1.17E05	5.83E-02mg/ml	-

Notes: 1. Precision is approximately ±4%

2. Total plutonium is calculated from known isotopic composition and hence specific activity of $^{239/240}$Pu per mg of Pu.

3. Precision is approximately ±4%

4. Plutonium concentration was measured by UV-visible spectrophotometry

4.2.3 Calculated mass of crystals and U and Pu hold-up ratios

The total mass of U in the crystals calculated from equation (1) is 25.22g.

Since the average U concentration in the scrubbed crystals (C-1, C-2 and C-3) is 0.488g/g, the total mass of damp crystals is calculated from equation (2) to be 51.65g. Since the average volume of scrubbed crystals is about 29mls, the apparent density of the damp crystals is 1.80g/ml. This density compares with a literature[5] value of 2.81 and indicates between 35% and 40% voids in the crystal bed.

The U hold-up ratio according to equation (3) is 0.57. The Pu hold-up ratio calculated by equation (5), from direct analysis of the crystals, is given below.

Table 4. Plutonium hold-up ratio in uranium crystals for MOX test 1, by equation (5) (cooled to 10°C).

Process step	Pu hold-up ratio
Initial separation	4.1E-02
First scrub	4.4E-03
Second scrub	2.3E-03
Third scrub	8.2E-04

It can be seen from Table 4 that the Pu hold-up was reduced from 4.1E-02 to 8.2E-04 by scrubbing.

4.2.4 Calculated DFs of crystals from Pu and main elements

The Pu DFs calculated from equation (6) and the DFs for the main elements calculated from equation (7) are given in Table 5 below.

Table 5. DFs for Pu and main elements for MOX test 1, (cooled to 10°C).

Sample		DF (see equations (6) and (7) in section 2.4 for definitions)							
		Pu	^{241}Am	^{244}Cm	^{134}Cs	^{137}Cs	^{154}Eu	^{155}Eu	^{125}Sb
Crystals	C-0	14	12	-	12	13	12	11	15
	C-1	126	103	-	61	101	100	98	27
	C-2	257	245	-	159	172	240	243	189
	C-3	681	829	887	667	743	906	862	418

Table 5 shows that Pu DF was similar to most of the main elements. The DFs for the actinides, Cs and Eu isotopes, for the final crystals varied between 667 and 906, and the corresponding DF for ^{125}Sb was 418.

4.3   MOX TEST 2

4.3.1   Crystallisation behaviour

The MOX solution started to crystallise at just below 28°C. This is seen in Figure 6 as a rise in solution temperature. The exotherm was more distinct than for the first MOX test possibly because the rate of decrease in solution temperature was somewhat lower, and even closer to the target (about –0.5^{o}C for MOX 2 compared between about –0.5^{o}C and –0.6^{o}C for MOX 1).

As was the case with MOX test 1, when temperature was decreased further, crystals were clearly evident and towards the steady-state set point of 0°C the solution had become less intensely dark green.

4.3.2   Volumes and chemical compositions of crystals and solutions

The measured volumes of the crystals and solutions are given in Table 6 below. The concentrations of U, Pu and nitric acid are also given in Table 6. Concentration in the crystals is given as mg/g of damp crystal.

The collected filtrate solutions and samples of crystals are shown in Photograph 8. The filtrate samples for both the MOX 1 and MOX 2 tests are shown in Photograph 9.

Table 6. Concentrations of U, Pu and nitric acid for MOX test 2, (cooled to 0°C).

Sample		Volume (mls)	U conc.	Pu conc.	Pu valence	HNO$_3$ (M)
MOX feed solution before crystallisation		92	456mg/ml	47.4mg/ml	(IV)	4.6
Scrub solution	1	50	156mg/ml	-	-	5.5
	2	50	156mg/ml	-	-	5.5
	3	50	156mg/ml	-	-	5.5
Crystals	C-0	38	472mg/g	6.97mg/g	-	-
	C-1	38	488mg/g	7.70E-01mg/g	-	-
	C-2	35	480mg/g	1.34E-01mg/g	-	-
	C-3	35	485mg/g	7.45E-02mg/g	-	-
Solution after crystallisation	L-0	57	234mg/ml	65.0mg/ml	(IV)	7.1
Scrub solutions after washing	L-1	50	165mg/ml	8.8mg/ml	-	6.1
	L-2	51	160mg/ml	1.1mg/ml	-	5.7
	L-3	51	153mg/ml	1.09E-01mg/ml	-	5.5

The data in Table 6 show that:

a) The average U concentration in the scrubbed crystals (C-1 to C-3 inclusive) is 0.484g/g which is about 2% above the theoretical stoichiometric quantity of 0.474g/g for pure UNH.

b) The volume of crystals did not vary significantly from the initial separation from the 'mother' liquor to the final scrub and averaged 36.5mls. As expected, this was higher than

for the MOX 1 test because the lower final temperature resulted in more U crystallising from solution.

c) The initial Pu concentration in the crystals was about a factor of 2 higher than for MOX 1, but decreased to a very similar concentration after three scrubs (i.e. 7.32E-02 mg/g for MOX1 and 7.45E-02mg/g for MOX 2).

As shown in Figure 7, UV-visible spectrophotometry confirmed that all the Pu (within the limit of detection corresponding to about 0.1% of the total Pu) was present as Pu(IV). The concentrations of the main elements, not including ^{244}Cm, are given in Table 7 below.

Table 7. Concentrations of main elements determined by gamma spectrometry* for MOX test 2, (cooled to 0°C).

Sample		Concentrations in Bq/ml for solutions and Bq/g for crystals					
		^{241}Am	^{134}Cs	^{137}Cs	^{154}Eu	^{155}Eu	^{125}Sb
Feed solution before crystallisation		1.96E08	1.92E06	5.47E08	6.02E06	4.81E06	1.63E06
Crystals	C-0	3.33E07	3.38E05	9.34E07	1.05E06	8.55E05	2.82E05
	C-1	3.62E06	4.11E04	1.02E07	1.14E05	9.20E04	3.15E04
	C-2	3.76E05	5.09E03	1.36E06	1.11E04	9.43E03	5.77E03
	C-3	1.24E05	1.66E03	4.33E05	3.11E03	3.53E03	4.53E03
Solution after crystallisation	L-0	3.08E08	2.98E06	8.21E08	9.56E06	7.89E06	2.39E06
Scrub solutions after washing	L-1	4.14E07	4.2E05	1.13E08	1.31E06	1.03E06	3.42E05
	L-2	4.71E06	4.86E04	1.30E07	1.49E05	1.19E05	3.94E04
	L-3	5.08E05	6.98E03	1.51E06	1.64E04	1.30E04	6.78E03

*Note: precision of analysis is generally approximately between ±1% and ±3% except for ^{125}Sb, which was ±5% for the L-1 and L-3 scrub samples and between ±7% and ±8% for the other samples.

The concentrations of $^{239/240}$Pu and ^{244}Cm, determined by alpha spectrometry, are given in Table 8 as follows.

Table 8. Concentrations of plutonium and curium determined by alpha spectrometry for MOX test 2, (cooled to 0°C).

Sample		Concentrations in Bq/ml for solutions and Bq/g for crystals		
		$^{239/240}$Pu[1]	Total Pu[2]	^{244}Cm[3]
Feed solution before crystallisation		-	-[4]	1.83E07
Crystals	C-0	1.39E07	6.97mg/g	-
	C-1	1.54E06	7.70E-01mg/g	-
	C-2	2.61E05	1.31E-01mg/g	-
	C-3	1.49E05	7.45E-02mg/g	7.81E03
Scrub solutions after washing	L-1	-	-[4]	-
	L-2	-	-[4]	-
	L-3	2.18E05	1.09E-01mg/ml	-

Notes: 1. Precision is approximately ±4%

2. Total plutonium is calculated from known isotopic composition and hence specific activity of $^{239/240}$Pu per mg of Pu.

3. Precision is approximately ±4%

4. Plutonium concentration was measured by UV-visible spectrophotometry

4.3.3 Calculated mass of crystals and U and Pu hold-up ratios

The total mass of U in the crystals calculated from equation (1) is 28.61g. As expected, this is somewhat higher than for MOX 1 because of the lower solubility of uranyl nitrate at 0°C.

Since the average U concentration in the scrubbed crystals (C-1, C-2 and C-3) is 0.484g/g, the total mass of damp crystals is calculated from equation (2) to be 59.11g. The average volume of scrubbed crystals is about 36mls, therefore the apparent density of the damp crystals is 1.64g/ml. This value is somewhat lower than the apparent density of the crystal bed for the MOX 1 test, which was 1.80g/ml.

The U hold-up ratio according to equation (3) is 0.68. The Pu hold-up ratio at each stage, according to equation (5), decreased from 9.4E-02 to 1.0E-03, as given in Table 9 below.

Table 9. Plutonium hold-up ratio in uranium crystals for MOX test 2, by equation (5) (cooled to 0°C).

Process step	Pu hold-up ratio
Initial separation	9.4E-02
First scrub	1.0E-02
Second scrub	1.8E-03
Third scrub	1.0E-03

The initial hold-up for MOX 2 is greater than for MOX 1 (9.4E-02 compared with 4.1E-02) but decreased to a similar level in the final crystals (8.2E-04 and 1.0E-03 for MOX 1 and MOX 2 respectively).

4.3.4 Calculated DFs of crystals from Pu and main elements

The Pu DFs calculated from equation (6) and the DFs for the main elements calculated from equation (7) are given in Table 10 below.

Table 10. DFs for Pu and main elements for MOX test 2, (cooled to 0°C).

Sample		DF (see equations (6) and (7) in section 2.4 for definitions)							
		Pu	^{241}Am	^{244}Cm	^{134}Cs	^{137}Cs	^{154}Eu	^{155}Eu	^{125}Sb
Crystals	C-0	7	6	-	6	6	6	6	6
	C-1	66	58	-	50	57	57	56	55
	C-2	372	549	-	397	424	571	534	297
	C-3	676	1682	2490	1230	1344	2059	1443	382

It can be seen from Table 10 that initial DFs were lower than for MOX 1 but final DFs were generally higher. However, the final DF for Pu (and ^{125}Sb) was slightly less than for MOX 1.

5 Conclusions

1. Spontaneous crystallisation of uranyl nitrate hexahydrate (UNH) in MOX solution occurred in both tests at approximately 28°C. This is less than the 32°C observed with pure uranyl nitrate/nitric acid solutions, possibly because of the presence of fission product impurities and plutonium (Pu).

2. The MOX 2 test with a final temperature of 0°C gave, as expected, a higher yield of UNH crystals than the MOX 1 test with a final temperature of 10°C. The U hold-up ratio (U in crystals as a proportion of the total U in the MOX feed to the process) was 0.57 and 0.68 for MOX 1 and MOX 2 respectively.

3. The hold-up of Pu in the UNH crystals (Pu in crystals by direct analysis as a proportion of the total Pu in the MOX feed to the process) was very low, with values for the final crystals after three scrubs of 8.2E-04 for MOX 1 and 1.0E-03 for MOX 2.

4. The U concentration in the damp crystals was very similar for both MOX 1 and MOX 2, at 0.488g/g and 0.484g/g respectively, which is within 2% - 3% of the theoretical stiochiometric ratio for pure UNH.

5. The good agreement of the U concentration in the crystals with that for pure UNH indicates that very little liquid was held up in the crystals after filtration. However, the quantity of actinide and fission product impurities scrubbed from the UNH crystals was relatively high, in terms of volumes and concentrations of the filtrate solutions. Therefore

scrubbing possibly leached the actinides and fission products from the UNH crystals, rather than diluted and removed liquid held up in the crystals.

6. High decontamination of the UNH crystals from Pu and the main actinide and fission product impurities was achieved by scrubbing. For example, DFs for ^{241}Am, ^{244}Cm, $^{134/137}$Cs and $^{154/155}$Eu were generally about 700 to 900 for MOX 1 and 1200 to 2500 for MOX 2. The DFs for Pu in the final crystals were similar for both MOX 1 and MOX 2, at just under 700. For MOX 2, the significantly lower DF for Pu than for the other actinides and fission products (except ^{125}Sb) might indicate that the mechanism of Pu hold-up in the crystals differs from that of the other radionuclide impurities.

7. The DFs for MOX 2 were lower for the initial crystals than for MOX 1 but were higher for the final crystals after three scrubs. The data on the volume and estimated weight of the crystal beds indicates that the density of the MOX 2 crystal bed was somewhat lower than for MOX 1. Hence, the MOX 2 crystals might have had a more open structure which resulted in an initial higher hold-up of impurities but more efficient leaching during the scrub process.

6   References

(1)   Applicability of crystallisation technology to nuclear fuel reprocessing. A Kurashima, H Fujihara, T Namba, K Suzuki, K Nishimura, M Hanzawa, S Yamagami. Proceedings of the Fourth International Conference on Nuclear Fuel Reprocessing and Waste Management, RECOD '94, vol. 1 (1994)

(2)   Uranium and plutonium refining by nitrate crystallisation. K Ebert and E Henrich. Nuclear Technology International P106, Sterling publ. Lit., London, Geary, N. Ed., (1988).

(3)   The Crystallisation of Pu(IV) in Nitric Acid. R. Cooke and C. Mason, AEAT/R/NS/0177 (2000).

(4)   The Crystallisation of Pu(VI) and Mixed U/Pu. R. Cooke and C. Mason, AEAT/R/NS/0369 (2001).

(5)   CRC Handbook of Chemistry and Physics, Editor–in-Chief Robert C. Weast, CRC Press, Inc. Boca Raton, Florida (66th Edition, 1985).

Appendices

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Appendix 1
Figures

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Figure 1. Crystallisation apparatus

Figure 2. Variation of temperature with time for uranium commissioning test, 10C

Legend:
Sample T
Coolant T
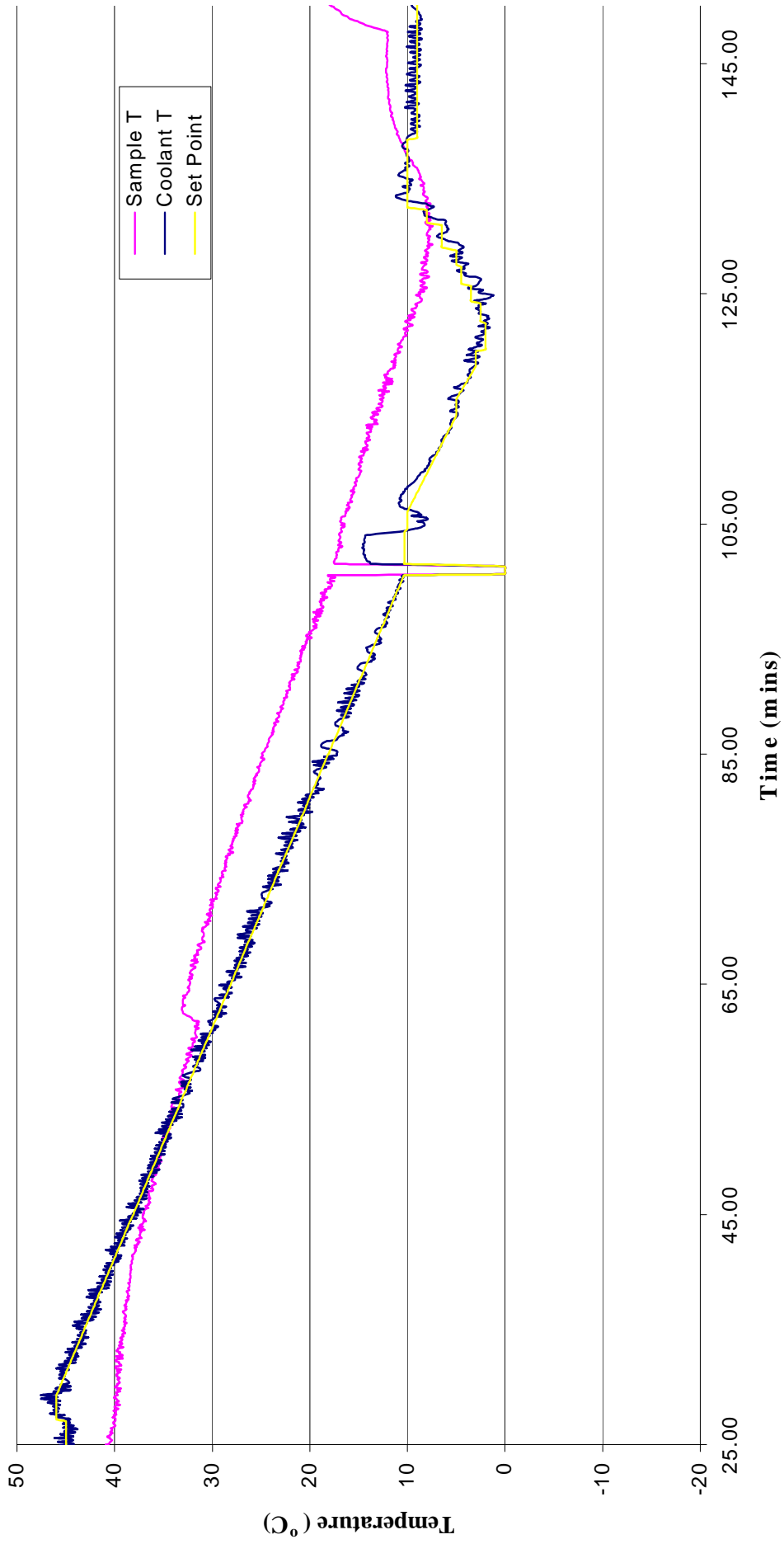Set Point

X-axis: Time (mins)
Y-axis: Temperature (°C)

Figure 3. Variation of temperature with time for irradiated MOX 1 test (PuIV), 10C
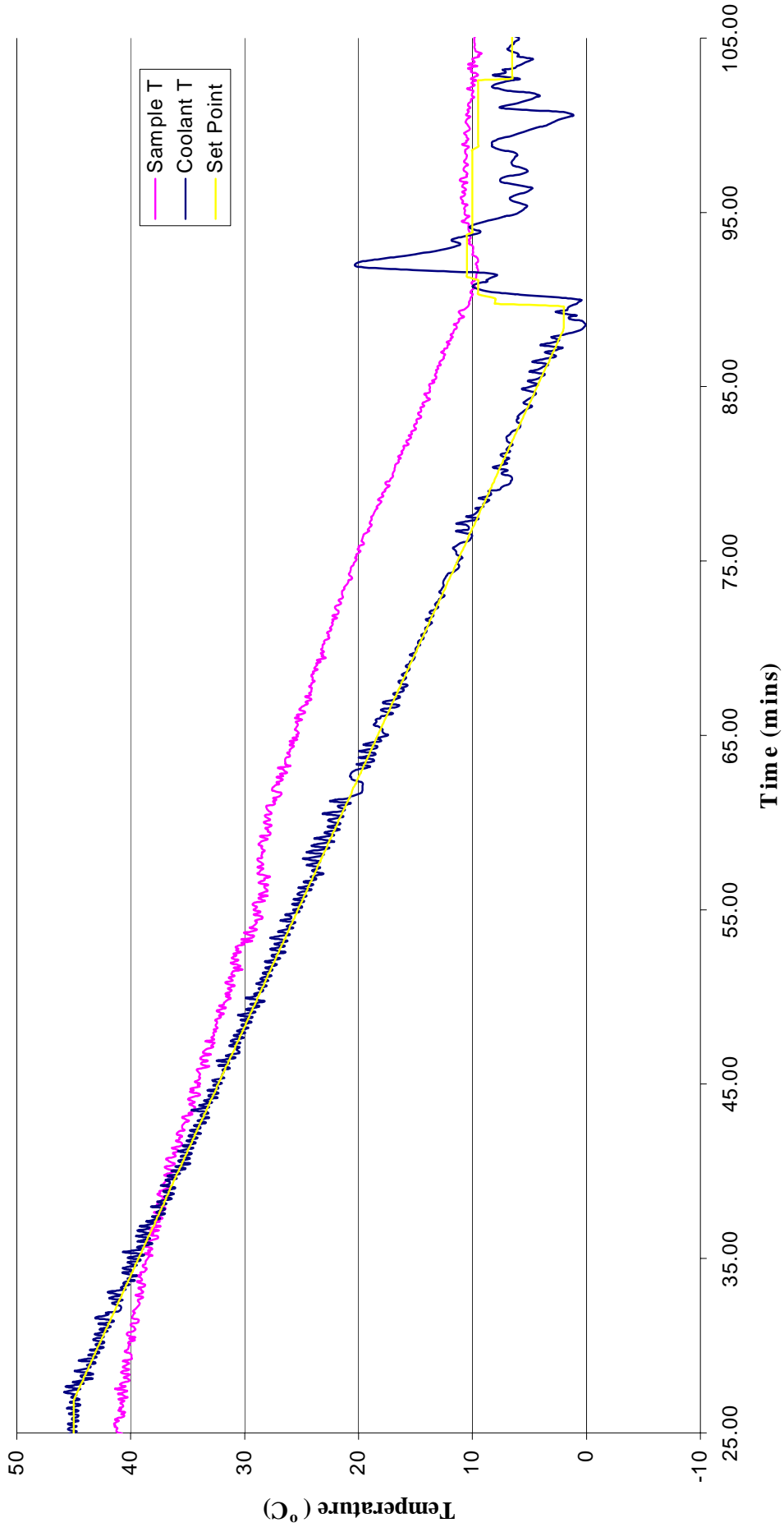
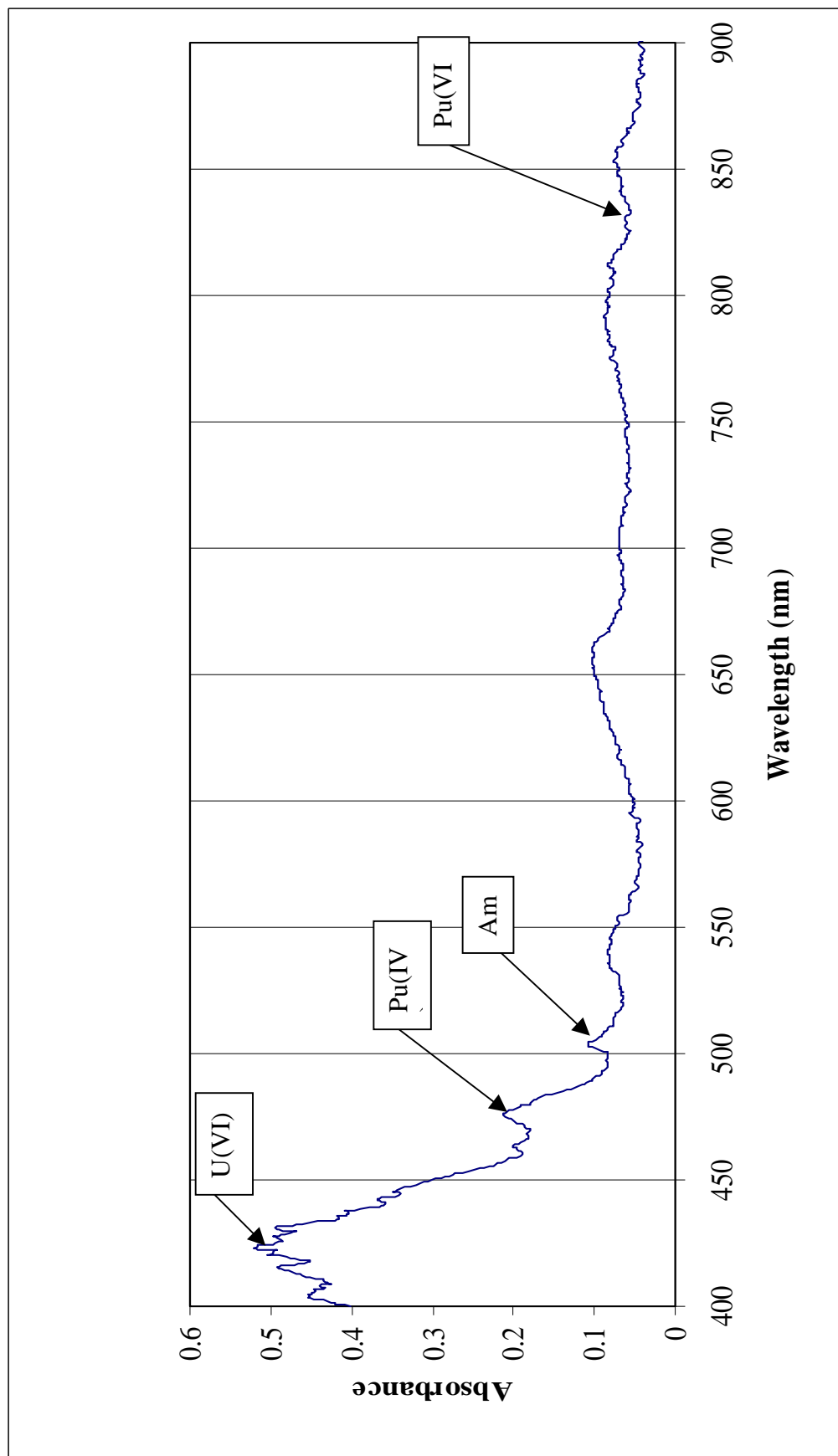**Figure 4. UV-visible spectrum for MOX feed to crystallisation**
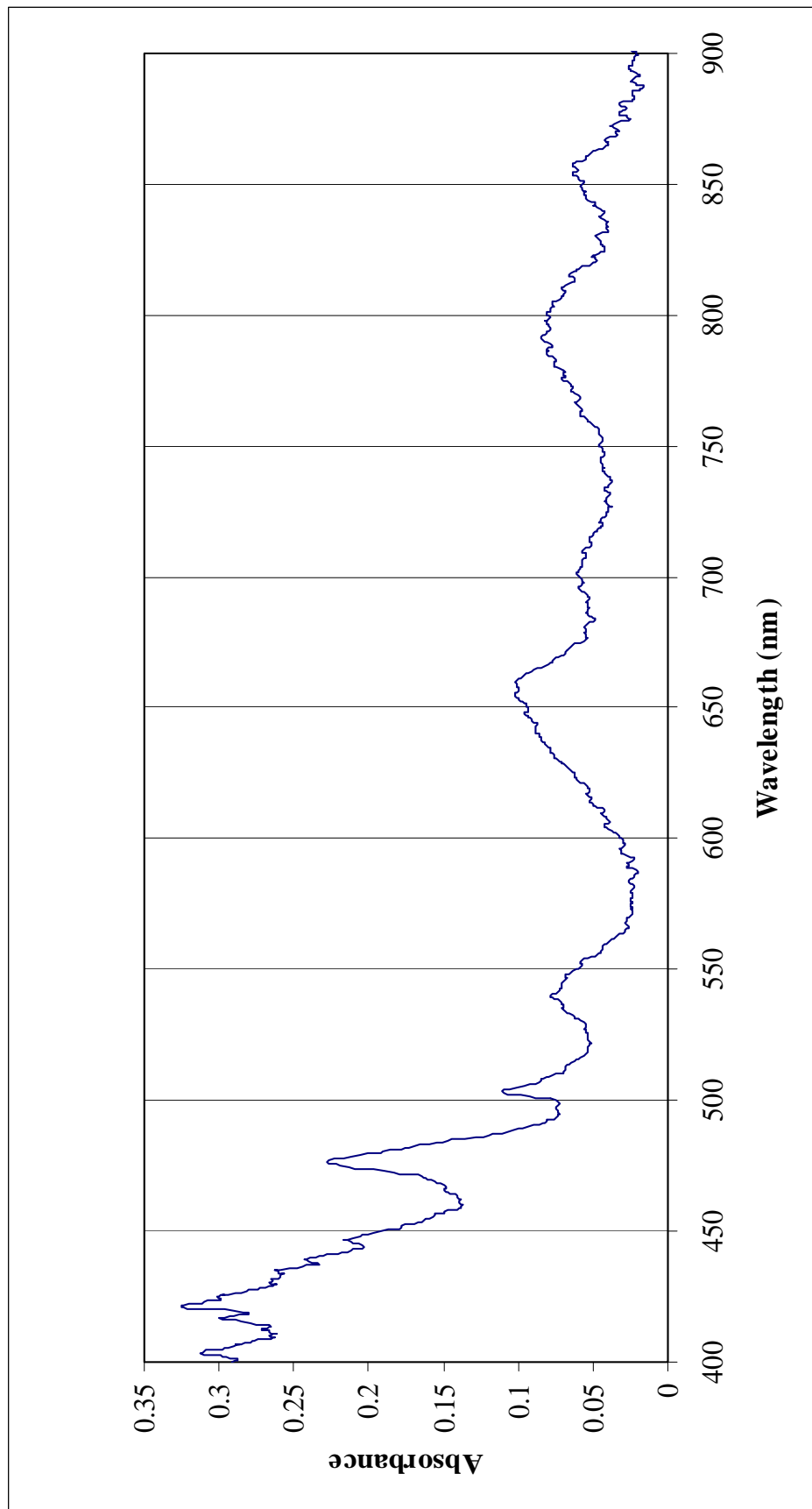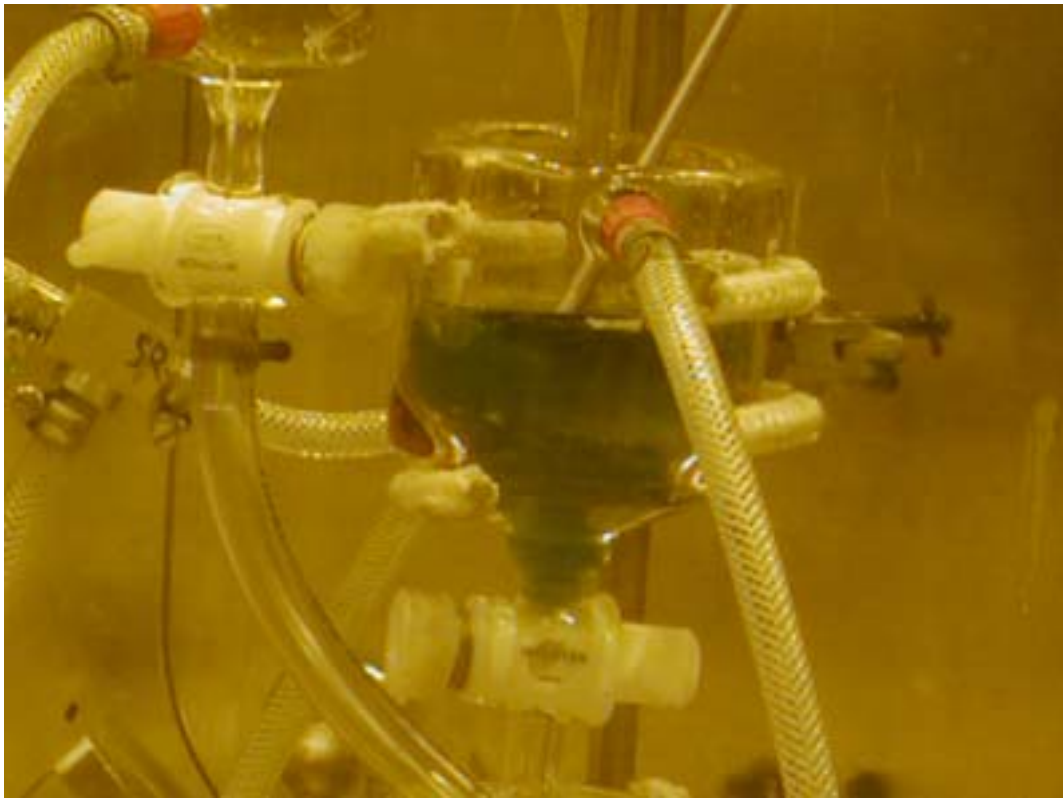
Figure 5. UV-visible spectrum for MOX 1 'mother' liquor

Figure 6. Variation of temperature with time for irradiated MOX 2 test (PuIV), 0C
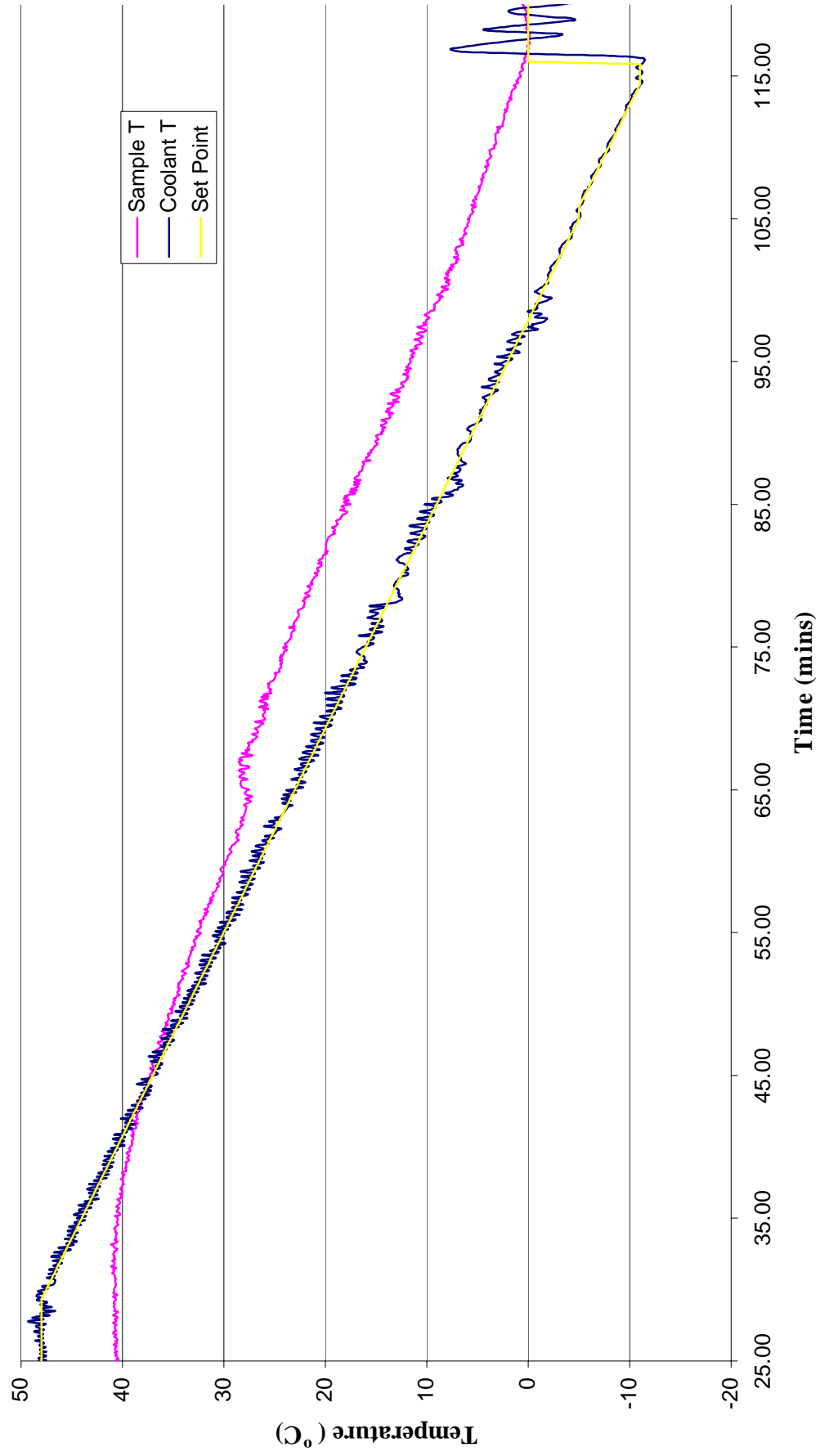
Figure 7. UV-visible spectrum for MOX 2 'mother' liquor

x
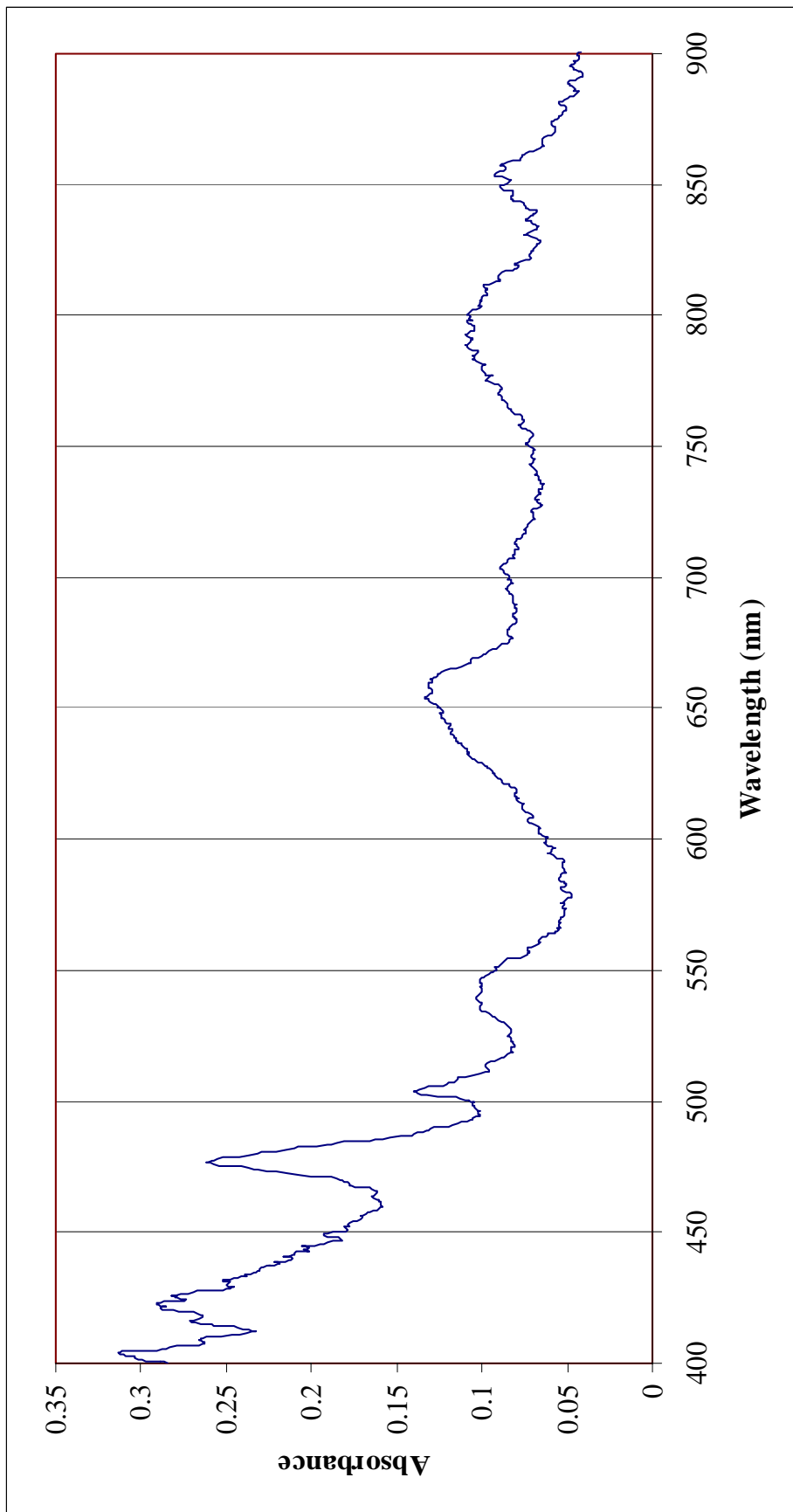
Appendix 2
Photographs

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Photograph 1. MOX crystallisation equipment in hot cell

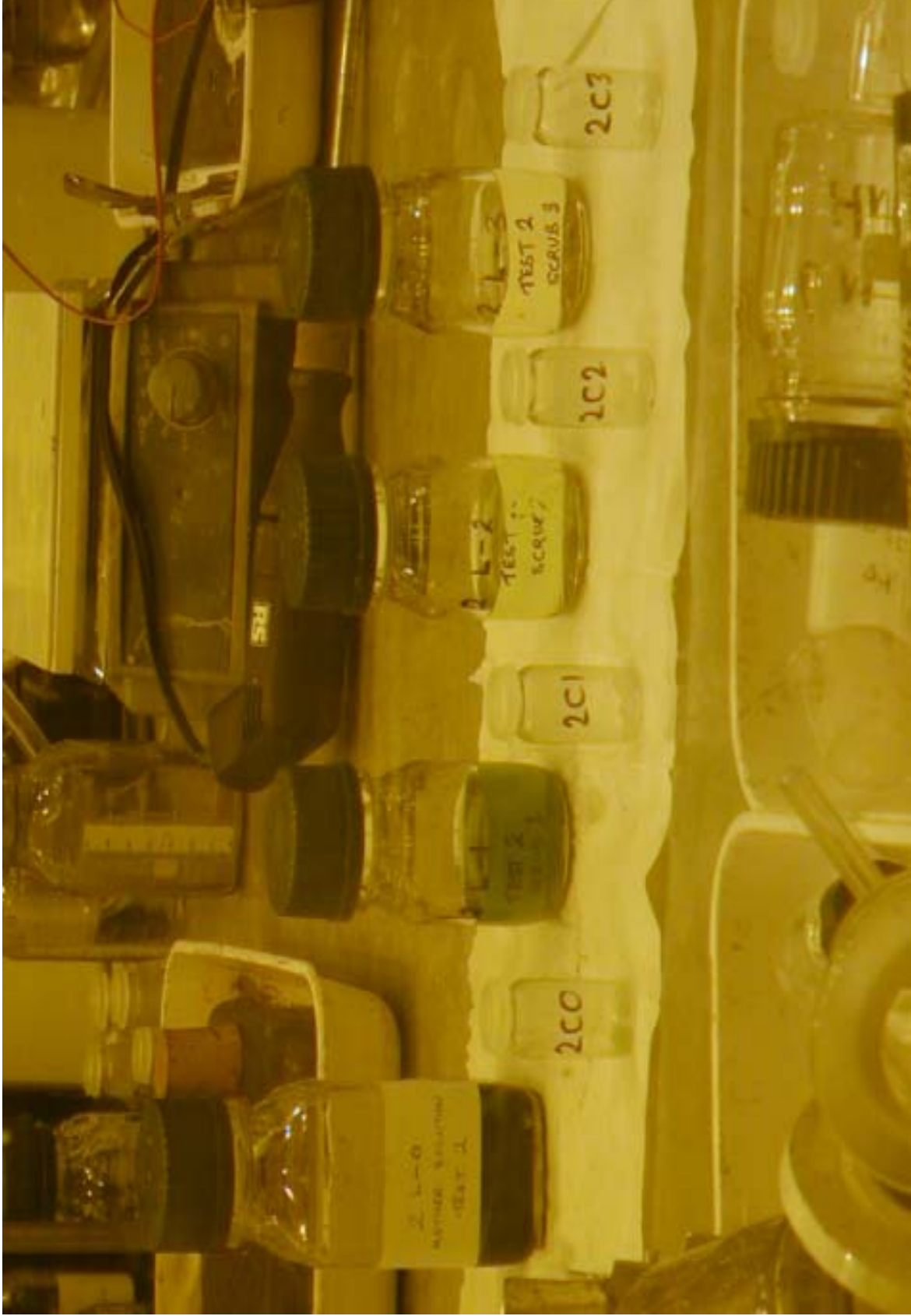**Photograph 2. Close-up of MOX solution in crystallisation vessel**
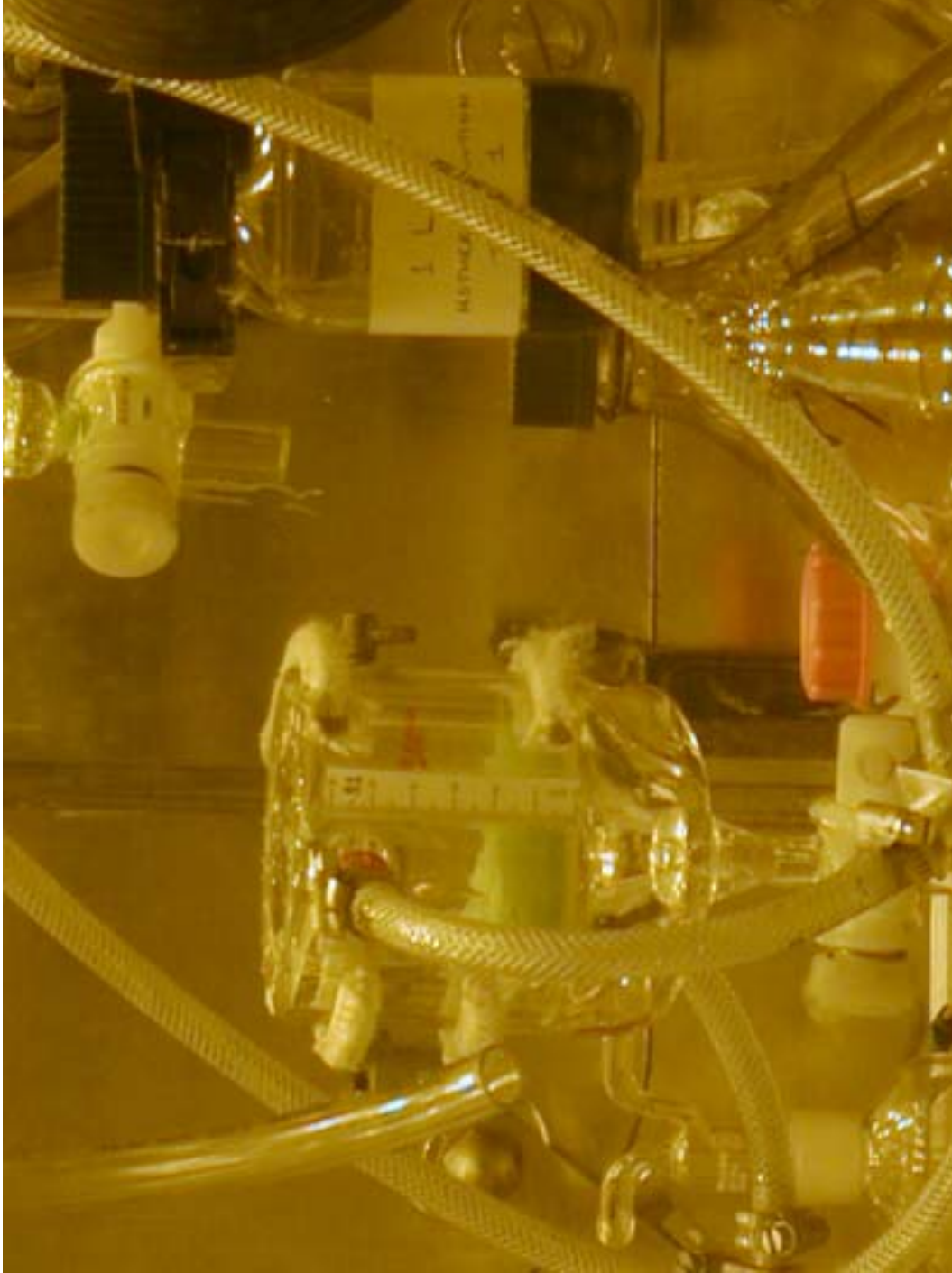
Photograph 3. MOX 1 crystals immediately after separation from 'mother' solution (liquid on right-hand side)
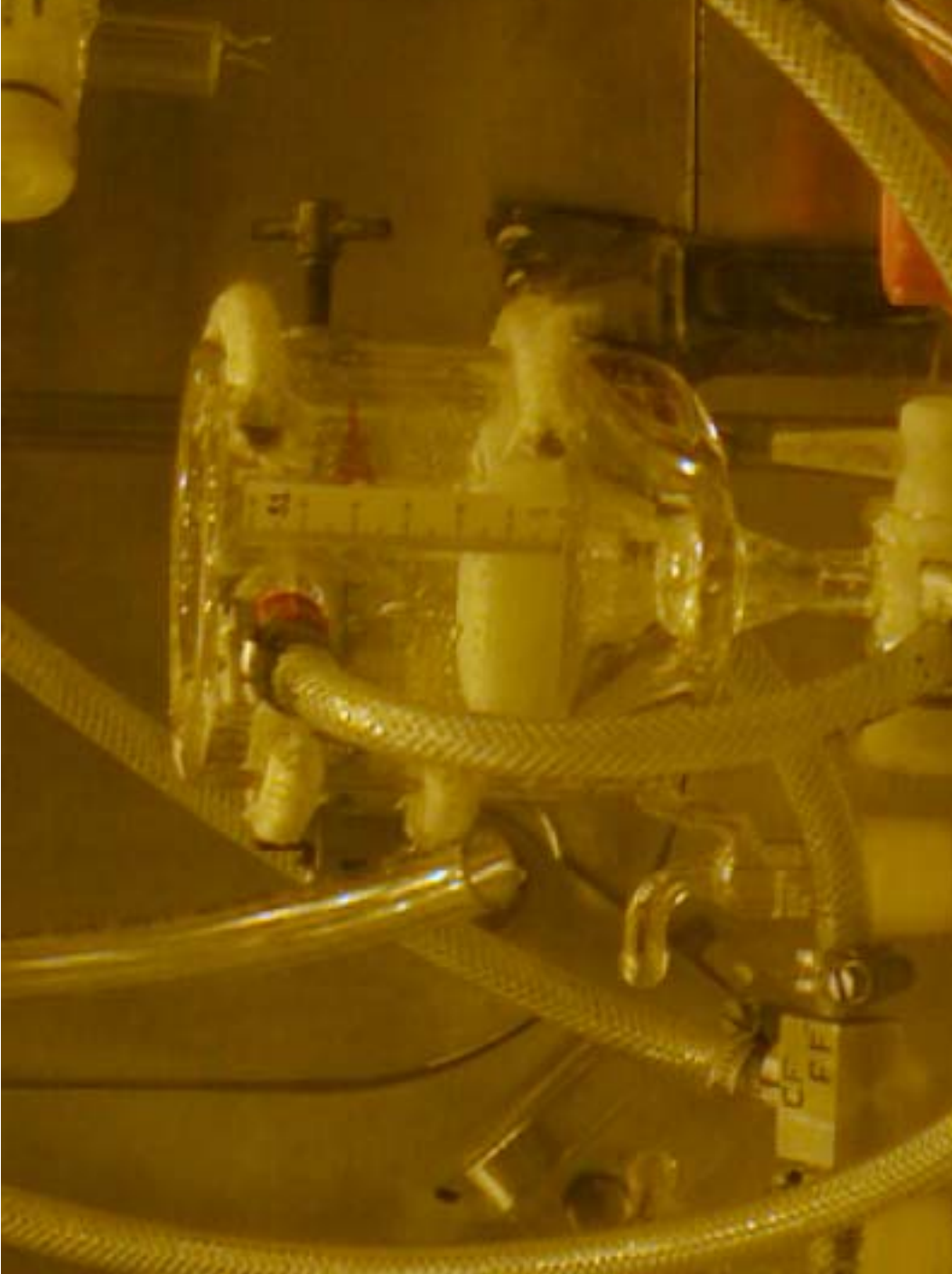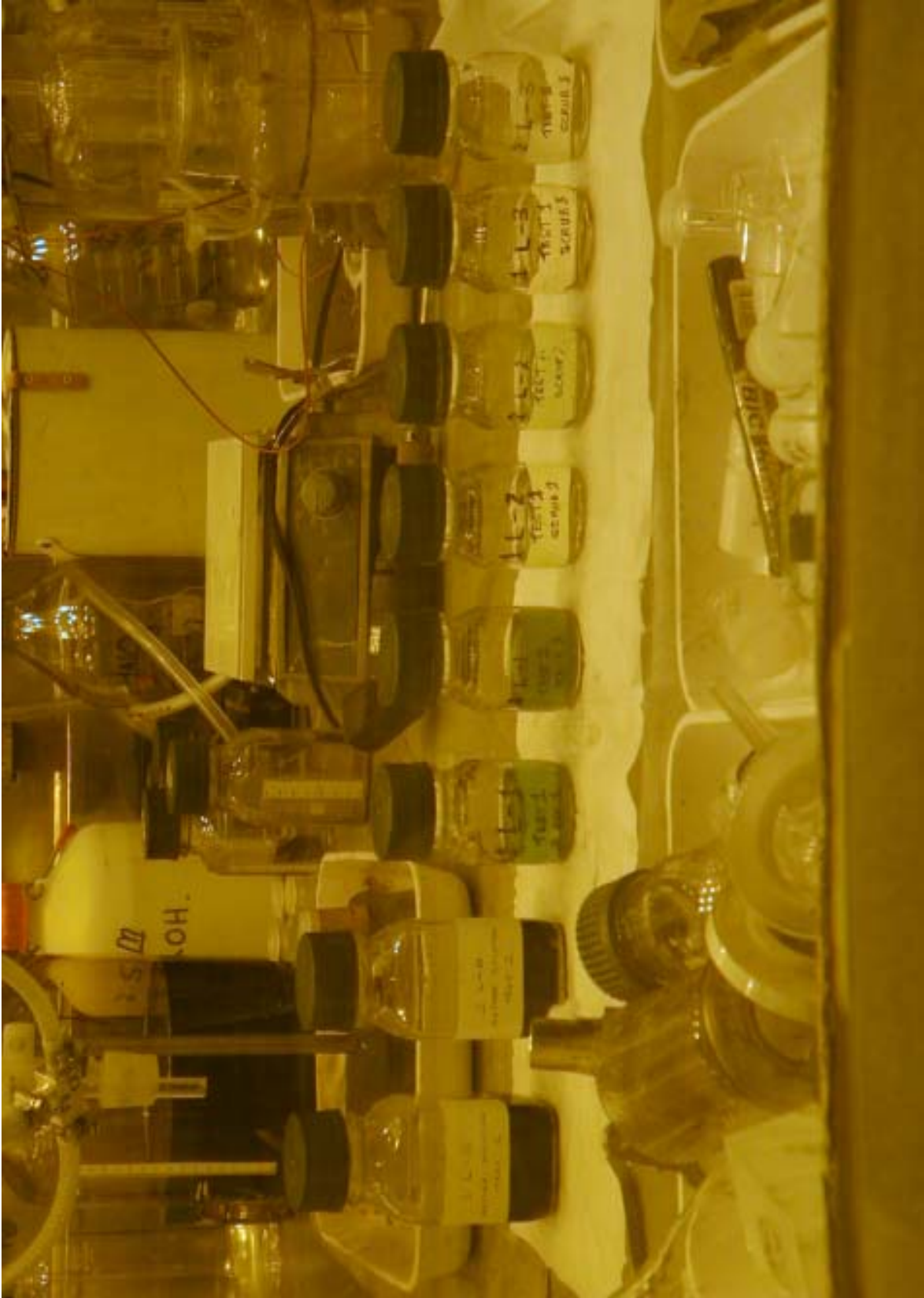
Photograph 4. MOX 1 crystals after third scrub (1 C-3)

Photograph 5. Filtered liquids and samples of crystals from MOX 1 test

Photograph 6. Filtered liquids and samples of crystals from MOX 2 test

Photograph 7. Filtered liquids MOX 1 and MOX 2 tests