PROCESSING OF THE MCC K26 PLUTONIUM-BEARING SLUDGES TO RECOVER WEAPONS-GRADE PLUTONIUM THAT IS NOT UNDER ANY TREATY OR MONITORING AGREEMENT

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ABSTRACT

Russian Federation (RF) and United States (US) collaborations from July 1998 through July 2001 conducted investigations of the Pu-bearing sludges in storage at the Mining Chemical Combine (MCC) K-26 site in order to dispose of weapons-grade plutonium and decommission the radiochemical plant. This RF work resulted in the recovery of approximately 20 kg of weapons-grade plutonium (and ~19 MT of uranium) from the sludges which was stored as oxide. Another method investigated and partially developed as joint collaborative efforts during this time period was direct immobilization of plutonium with no recovery of plutonium. This method melts the untreated recovered sludges by microwave ultrahigh frequency (UHF) heating with glass formers. After cooling, melter-crucibles of vitrified sludge are stored on site in underground cavities for eventual disposal in a geologic repository.

Cost and technical feasibility studies of the two methods show that direct immobilization (i.e., vitrification)of the plutonium-containing sludge is the preferred alternative. It is also preferred from the ecological point of view. However, RF funding alone is insufficient to continue this work, and US funding has been suspended. It appears unlikely that development of full scale vitrification technologies for the plutonium-bearing sludges can be undertaken without continuing support from the US or from others. Thus, the only demonstrated technology for the MCC for removing weapons-grade plutonium in sludges will remain recovery and extraction of plutonium for storage and reuse for the indefinite future. It is estimated the about 1200 to 1800 kg of weapons plutonium are in the sludges that must be removed an d treated as part of the MCC facility decommissioning. This specific plutonium is not covered under any current monitoring or treaty agreement between the RF and the US.

INTRODUCTION

A total of about 6000 m^3 of radioactive plutonium-containing sludges have been accumulated in liquid radioactive waste storage tanks during the entire 40-year period of weapons-grade

plutonium production at the radiochemical plant (RP) of the MCC at K26. These waste sludges were originally estimated in the fall of 1997 to contain approximately 600 kg of weapons-grade plutonium as part of joint US-Russian plutonium disposition studies. The results of tests made with retrieved sludges in years 2000 and 2001 found higher sludge density values than had been previously assumed, and a higher value of the relative weapons-plutonium content. Hence, the plutonium initial estimate of 600 kg is two to three times underreported [1,2,3].

The MCC sludge storage complex consists of seven storage tanks sited deep underground at the MCC in gneiss rock. Each tank has a 3000-m^3 capacity with varying quantities of radioactive sludge in the tank bottoms. Each tank is a reinforced-concrete cylindrical reservoir 30 m in height and 12 m in diameter, clad with stainless-steel plate on the inside. The tanks are utilized as part of the operating MCC radiochemical plant for (1) clarifying liquid alkali-nitrate-based intermediate level wastes, (2) decanting the clarified portion of wastes for disposal in an underground deep borehole area, and (3) storing the solid phases (i.e., the sludges) for the long term. The in-tank residue layers differ in thickness (4-22 m), composition, and density but all residues contain weapons-grade plutonium. After liquids are placed into the tanks, residues or sludges accumulate due to sedimentation of solids from the mixtures of saturated liquids, almost insoluble compounds, absorbents from plutonium purification, and sediments from uranium regeneration from irradiated nuclear fuel. Sludges accumulated in the tanks contain weapons-grade plutonium, uranium, and some radionuclides, but also corrosion products and aluminum hydroxides, polymerized forms of silicic acid, niobium oxide (V), manganese oxide (IV), used ion-exchange resins, and compounds of metals with tributylphosphate decomposition products.

The plans for decommissioning the MCC radiochemical plant include removing these plutonium-containing sludges from the tanks, processing the retrieved sludges to recover the plutonium and uranium in the radiochemical plant, and solidifying the radioactive components. Then the empty underground tanks are decontaminated and deactivated. This concept for handling these radiochemical plant waste sludges was first developed in Russia at the end of the 1980s; it consists of the following basic activities:

- Agitation and retrieval of sludge from tanks;
- Extraction of the basic portions of uranium, plutonium, and other long-lived radionuclides from the sludge into a liquid;
- Processing the liquid to extract and recover as oxide pure uranium and pure plutonium with the subsequent removal of the raffinates that arise for disposal;
- Solidification of insoluble residues;
- Temporary storage of solidified wastes;
- Geologic disposal of solidified wastes.

Figure 1 shows the baseline principle flow diagram of that illustrates this concept of radioactive sludge processing at the MCC to recover the weapons-grade plutonium and uranium for storage.

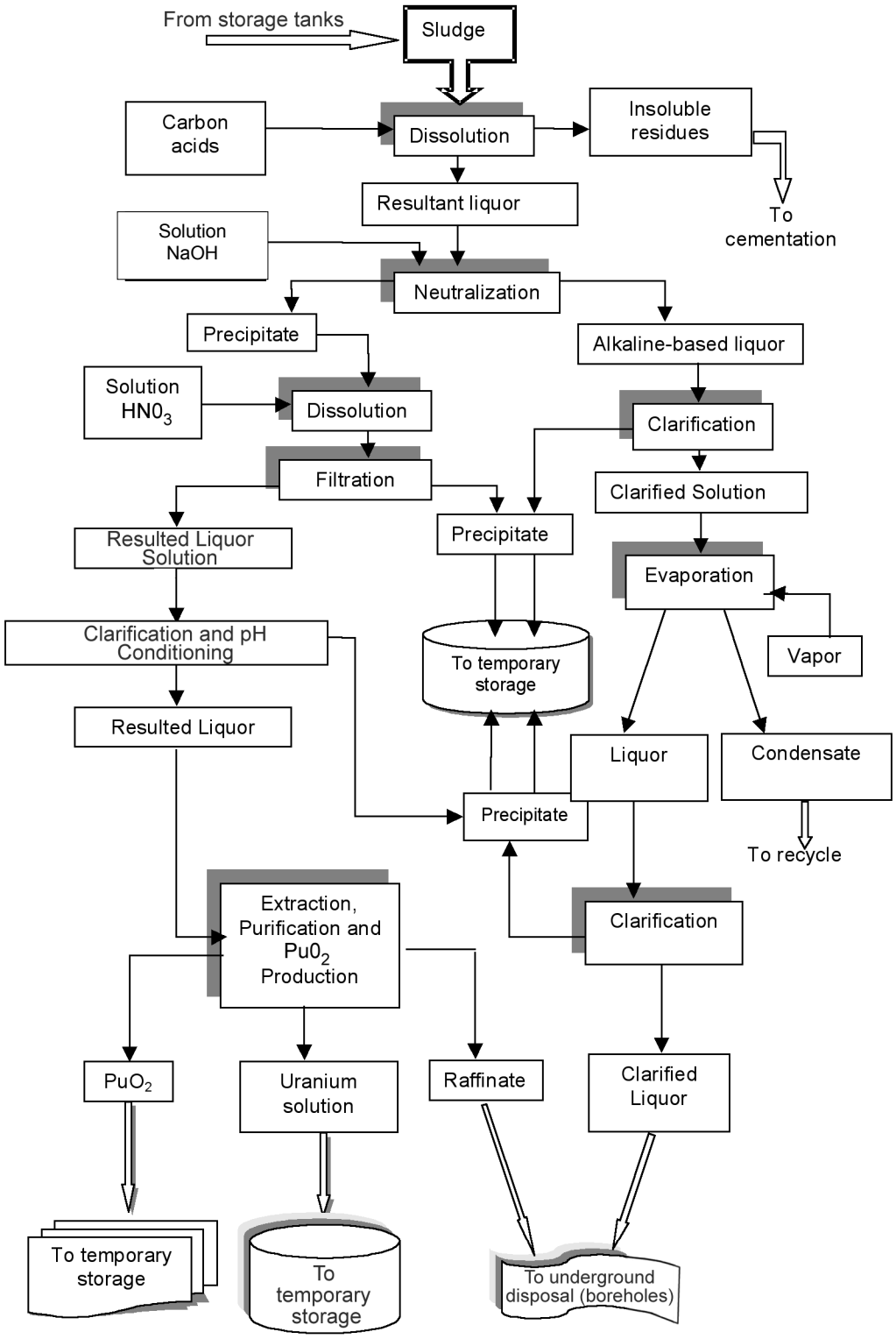

Fig. 1. Block diagram of Pu-bearing sludge plutonium and uranium extraction, purification, and recovery for storage.

MCC SLUDGE PROCESSING EXPERIMENTS TO RECOVER PLUTONIUM AND URANIUM

MCC began the actual development of practical industrial-scale activities for recovering and eliminating radioactive sludges at the MCC in 1996. Sludge retrieval equipment was mounted into a 3000-m^3 tank, and between January 1996 and June 1998, while testing, a total of about 80 m^3 of the most active and movable sludge was removed. From June 1998 through July 2001, an additional 350 m^3 of sludge was retrieved.

MCC found that sludge residues, when subjected for many years to high temperature and radiation fields, are compacted. The solid particles are incorporated into a spatial framework, and the sludges have lost their fluidity. The analysis of samples taken from one tank shows that the stored sludges may be conditionally divided into the three following layers with no clear boundaries:

- An upper movable layer with solids concentration of up to 60 g/l;
- A middle layer of condensed plastic sludge with solids concentrated at up to 120 g/l; (with vigorous stirring for a long time period, this layer can be destroyed and suspended);
- A dense layer of sludge at the bottom that is de-watered due to radiolysis, and in which solids are concentrated at up to 800 g/l.

The original retrieval equipment was found to operate with less efficiency near the bottom when the barely movable and more dense layers of sludge were exposed. There was a significant decrease in the solids in the retrieved sludge slurries. It became obvious that the dense layer of sludge could not be removed with the original equipment in use without having to destroy the dense sludge layer. As a result, the sludge retrieval equipment was modified, tested, and chemical treatments applied. This new equipment allowed removal of about 85% to 90% of the sludge from the tank. Unfortunately, some solid sludge constituents carried over into the liquors and this needs further development work. The uranium solids, in part, dissolved during the use of chemicals to assist retrieval, via dissolution of the cross-linked and partially vitrified [aggregated] solids. To retrieve sludges from the bottom dense layers is quite a serious problem but MCC has now developed, tested, and demonstrated the technologies needed to do this.

Figure 2 illustrates the equipment setup for sludge retrieval from storage tanks. Table I lists some basic constituents in retrieved sludge and some physical characteristics of sludge.

During tests conducted from July 1998 until May 2000, while applying chemical treatments, MCC retrieved a total of 12 kg of weapons-grade plutonium, 19,400 kg of uranium, 1,120 kg of aluminum, 1,010 kg of iron, 5,500 kg of manganese, 150 kg of chromium, and 540 kg of silicon. From May 2000 until July 2001, an additional 8 kg of weapons plutonium was recovered as oxide and put into storage [2].

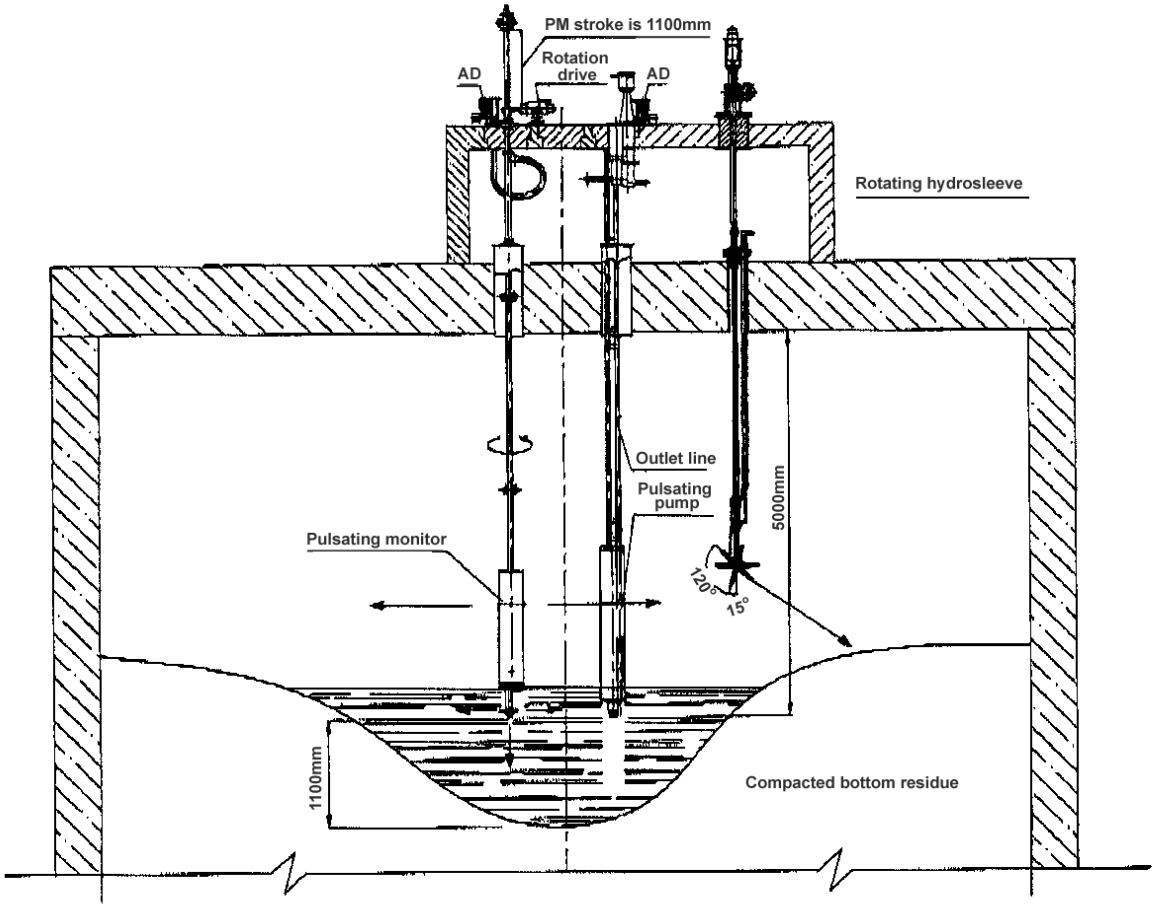

Fig. 2. Equipment setup for sludge retrieval from MCC storage tank.

Table I. Characteristics of sludge retrieved from storage tank at MCC.

Constituent or property	Unit	Value
Uranium	g/l	19.7
Plutonium	mg/l	54.9
Iron	g/l	20.4
Manganese	g/l	41.0
Chromium	g/l	0.6
Aluminum	g/l	2.2
Silicon dioxide	g/l	3.9
β-activity	Ci/l	2.3
Exposure Dose Rate	μR/l s	13.3
Sludge density	g/cm^3	1.20
Solids concentration	g/l	123.2

MCC SLUDGE PROCESSING EXPERIMENTS WITH NO PLUTONIUM RECOVERY AND DIRECT IMMOBILIZATION

In 1998-1999, as part of joint US-Russian plutonium activities under contract B347676 (started 6/4/98) with Lawrence Livermore National Laboratory (LLNL), MCC performed a technical and economic engineering feasibility (TEF) study and developed an alternative processing method for sludge. This method provided for the direct immobilization of the sludge into glass matrices with no extraction of plutonium and uranium for recovery and storage as oxides. Comparative cost assessments conducted as a part of the engineering feasibility study have shown that the proposed direct immobilization alternative processes provide numerous cost and secondary waste minimization advantages compared to the baseline plutonium recovery process provided that the plutonium and uranium have no immediate use or known product monetary value [1].

In 1999-2000, under a second contract B506210 (started 11/4/99) with LLNL, MCC developed and issued a Declaration of Intent (DOI) that was signed and approved by local and regional government authorities. The Russian DOI is basically equivalent to portions of the US DOE ROD and NEPA process for nuclear projects and is required in Russia for new projects. The DOI recommended stopping the development of reprocessing of sludges to recover plutonium from the sludges as oxide for storage as the baseline radiochemical plant decommissioning option. Instead, the DOI recommended the development of an immobilization vitrification option, either a borosilicate and a phosphate glass, for direct solidification of the sludges with no recovery of plutonium and uranium.

In 2000-2001, under a third contract B506233 (started 7/4/00) with LLNL, MCC performed a detailed Justification of Investment (JOI) for these two vitrification options. A Russian JOI is equivalent to developing a facility engineering design that is somewhere between a detailed conceptual design and a preliminary (or Title I) design that also includes developing life cycle cost estimates, preliminary environmental assessments, and preliminary safety analyses. The final JOI is now being reviewed and approved by Russian organizations. The JOI will select a single borosilicate glass for the immobilization matrix and recommend stopping further development of a phosphate glass matrix in the next working design (TEO) phase based on economics, secondary wastes, environmental impacts, and radiation exposures.

Direct solidification and immobilization of the plutonium-containing sludges into either a (1) borosilicate or a (2) phosphate glass matrix were considered and developed in the TEF, DOI, and JOI. Costs and construction schedules were minimized by using to the maximum extent possible parts of the existing radiochemical plant and other existing MCC infrastructures. The solidification of radioactive sludges involves the following general stages:

- Sludge concentration by evaporation;
- Denitration;
- Drying;
- Calcination;
- Melting;

- Melt cooling;
- Annealing.

The MCC melting method uses microwave heating for the vitrification process in a hot cell [1]. The process operations can be performed directly in a microwave heater where the pour canister is also the melter chamber. A crucible-melter filled with vitrified sludge in this case serves as a container for long-term waste storage. After completing vitrification, the filled crucibles are transferred for packing into larger canisters (one crucible for one canister) and canister lids are seal-welded. Following the inspection of outer canister surfaces for radioactive contamination, the canisters are transferred to long-term storage into one of five reinforced-concrete cylindrical tanks, 30 m in height and 12 m in diameter. These tanks are located in a radiochemical plant chamber that has been refitted for a vitrified waste storage facility. The storage facility has room for 6800 canisters of 0.1 m^3 capacity, each with sludge immobilized into borosilicate glass, or for 11,860 canisters of 0.1 m^3 capacity, each with sludge immobilized into phosphate glass. The canisters are eventually removed and sent to a geologic repository. Figure 3 shows the flow diagram of MCC's industrial-scale processing of plutonium-bearing sludge with vitrification.

In summary, MCC has developed engineering details and performed melter hot cell immobilization tests with sludges in past three years to develop a feasible immobilization technology for their site [2,3]. The cost estimates and other measures have led the MCC to conclude that direct immobilization of the sludges into a borosilicate glass is their preferred alternative to extraction and recovery of plutonium for storage only. The TEF, DOI, and JOI participants are an integrated team of Russian experts from the MCC K-26, the Khlopin Radium Institute (KRI), the Bochvar All-Russian Scientific Research Institute of Inorganic Materials (VNIINM), the All-Russian Planning and Design, Research and Technological Association (VNIPIET), the Design Institute of Installation Technology (NIKIMT), and the All Russian & Design Institute of Production Engineering (VNIPIPT) [3].

CONCLUSIONS

The MCC K-26 work in these three LLNL contracts is accomplishing the US policy objectives of plutonium disposition and nonproliferation, including discouragement of reprocessing. Currently, the K-26 MCC work is not planned to continue beyond the JOI phase. This is due to new DOE guidance for 2001 that the Russian immobilization work is suspended indefinitely and no new contracts are to be issued by LLNL. Therefore, the final direction of the MCC K-26 site toward recovering the weapons plutonium in the sludges as oxides for storage will remain unknown with the suspension of the initial work and the US technical interactions on immobilization technologies suspended.

Furthermore, during the tour for LLNL at K-26 on July 11, 2001, the MCC confirmed that about 20 kg of weapons plutonium has been recovered and separated to date as part of MCC RF activities. This amount has been recovered as a result of technological solutions and sludge tests made from a pilot scale or demonstration tank. The MCC has firmly established the feasibility of their recovery processes. In addition, MCC learned that their initial estimates of 600 kg of weapons plutonium in the K-26 MCC sludges is likely low by a factor of two to three times

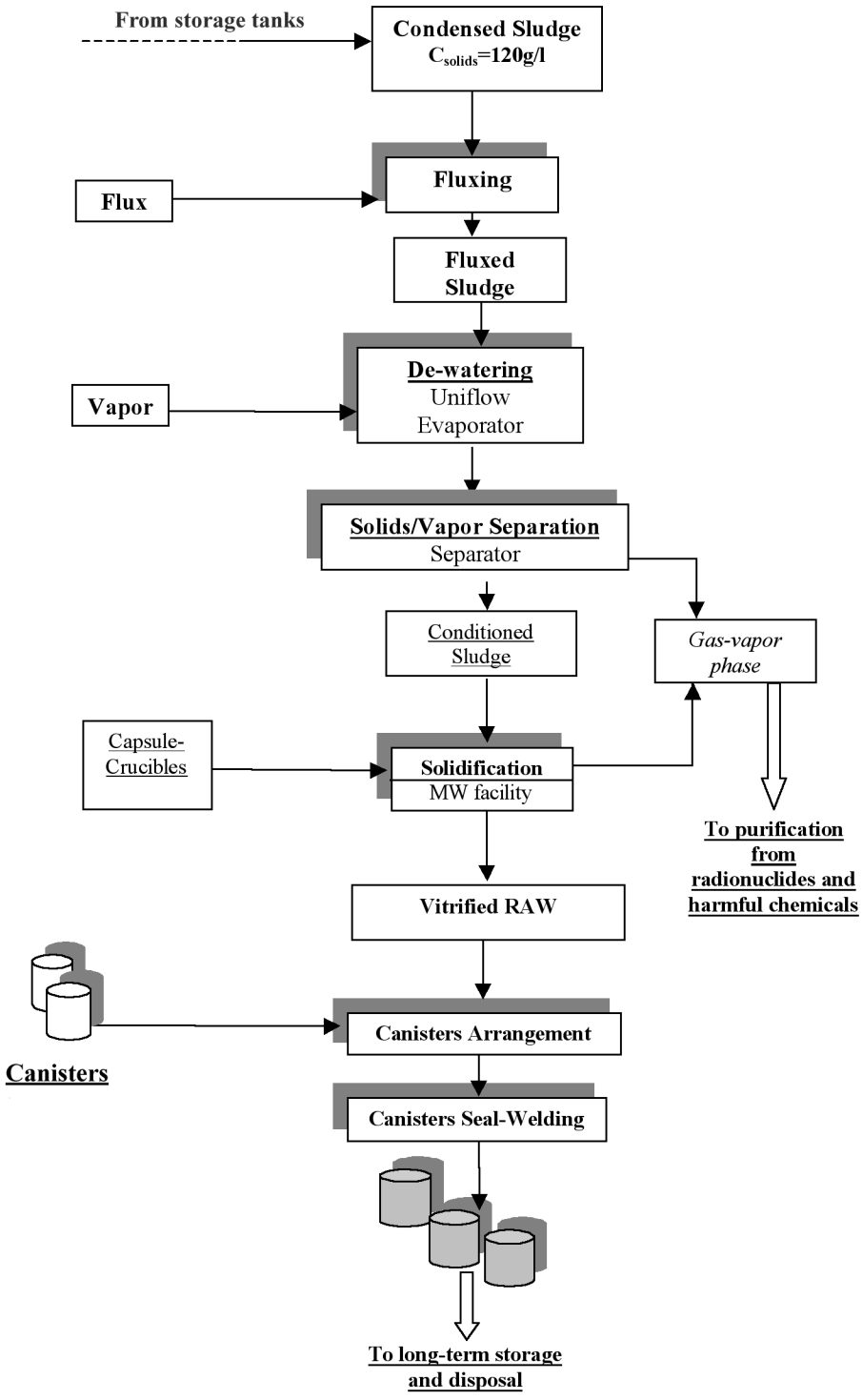

Fig. 3. Flow diagram of MCC industrial-scale processing of Pu-bearing sludge with vitrification and no recovery of plutonium and uranium.

because the sludge is of a higher density and plutonium content than initially predicted when the US-Russian joint work started in 1997.

MCC would prefer to continue the development and implementation of immobilization technologies for their plutonium-containing sludges but lack the funds to move alone into the next engineering and development phase, the TEO, without US or other funding. It is recommended that the US or others seriously consider providing the funding the MCC's direct immobilization option, and allow this remarkable and rapidly moving joint US-Russian project to continue without any interruption.

ACKNOWLEDGEMENTS

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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