Chapter 2
R&D on Cementation of Pulp with Complex Physical and Chemical Composition Stored in Tanks at the Mining Chemical Combine

L.P. Sukhanov, K.P. Zakharova, N.A. Naumenko, O.N. Pogorelko, A.V. Lebedeva, Yu. A. Revenko, V.A. Kravchenko, and V.I. Matselya

1 Introduction

Cementation is the basic technology for liquid LLRW/ILRW immobilization in the Russian Federation. In particular, the cementation technology will be implemented at the Mining Chemical Combine (MCC) in Siberia.

The object of cementation at MCC is “legacy waste,” i.e., of radioactive hydroxide pulps (HP) have been accumulated in the MCC storage tanks. These pulps are a result of previous activities of the MCC radiochemical plant. The volume of pulp—several thousands of cubic meters.

The MCC radiochemical plant is to be decommissioned in the near future. Accumulated pulps will be removed from the tanks and sent for cementation.

The aim of this report is to provide brief information about R&D results relevant to the above issue.

The management of pulp includes the following stages:

Stages being currently implemented

- Removal of liquid phase from storage tanks.
- Dissolution of pulp solid phase.
- Extraction of U and Pu from solutions (if appropriate).
- Collection of undissolved pulp residues in interim tank (as “secondary” pulp).

Stages planned

- Immobilization of undissolved pulp residues (“secondary” pulp) in a cement matrix.
- Long-term storage/disposal of cement compound.

L.P. Sukhanov (✉) • K.P. Zakharova • N.A. Naumenko • O.N. Pogorelko • A.V. Lebedeva
A.A. Bochvar High-Technology Research Institute of Inorganic Materials, Moscow, Russia
e-mail: lpsoukh@bochvar.ru

Yu. A. Revenko • V.A. Kravchenko • V.I. Matselya
The Mining Chemical Combine, Krasnoyarsk Region, Russia

F. Bart et al. (eds.), *Cement-Based Materials for Nuclear Waste Storage*,
DOI 10.1007/978-1-4614-3445-0_2,

The use of cementation technology for MCC pulp immobilization is based on different factors: ability to hold U and Pu in a cement compound, possibility to enhance ^{137}Cs confinement in a cement compound using sorbent additives, the process is carried out at low temperature and does not require sophisticated equipment, availability and relatively low cost of matrix materials, and absence of secondary waste.

^{137}Cs and ^{239}Pu in pulp are "critical" radionuclides for safety of long-term cementitious pulp storage. Safety of cement compound long-term storage/disposal facility is based on several barriers: matrix composition (cement + sorption additives), container (200-L drums) and packaging elements, engineering barriers of the storage/disposal facility (building structures, buffer materials, and sealing elements), massive rock materials between the storage/disposal facility and environment (the facility is located at a depth of ~200 m below the surface).

Main components of pulp sent for cementation include Fe_2O_3, Fe_3O_4, AlO(OH), Cr_2O_3, MnO_2, SiO_2, Ni and Sr and Cs (as hydro aluminum silicates), PuO_2 as silicates, aluminates, aluminum silicates, U as polyuranates.

Content of solid phase in the pulp is 100 ± 60 g/L, β-activity (mainly ^{90}Sr) is 1 ± 0.5 Ci/kg.

Pulps have multicomponent chemical composition with significant content of long lived alpha-radionuclides. Some components of the pulp solid phase can react with cement components (hydrated oxides of Fe, Al, Mn, Ni, and Cr).

Main objectives of investigations were to obtain experimental data to make recommendations on production of cement compounds satisfying the national waste acceptance requirements and to check possibility for using the facility with a pulse mixer for pulp cementation (new type of a cementation facility).

Scope of research investigations includes determining the characteristics of the produced cement compound (mechanical strength, water resistance, frost resistance, flowability, heat release, loading capacity of waste and others), assessing behavior of cement compounds during their production, and short-term storage and testing of the facility equipped with a pulse mixer for cementation of MCC pulp.

Main investigations have been performed using the simulated radionuclide-containing pulp. A set of experiments performed using the real pulp samples has been conducted at the Central radiochemical plant laboratory of MCC. All facilities and equipment available included pilot cementation facilities, laboratory equipment, radiation control instruments, and other equipment used at A.A. Bochvar Institute and MCC.

2 Procedure of Experiments

In laboratory conditions at VNIINM, there has been a wide range of experiments carried out using the hydroxide-pulp simulators. The experiments were meant to develop optimal parameters for the cementation process to ensure obtaining the required quality cement compound.

Table 2.1 Composition of hydroxide pulp simulators

	Components of undissolved pulp residue (wt%)	
Pulp component	Pulp simulator No. 1	Pulp simulator No. 2
$Al(OH)_3$	11.3	9.1
$Fe(OH)_3$	27.8	22.5
$Cr(OH)_3$	2.3	1.9
$Mn(OH)_2$	38.1	30.8
$Ni(OH)_2$	14.2	11.4
SiO_2	6.3	24.3

In the course of the research investigations, the following characteristics indices were determined: mechanical strength (after 7, 14, 28, 56, and 90 testing days), water resistance and frost resistance of a cement compound, radionuclide leaching rate, flowability, and specific heat release during hydration of compounds.

Two types of pulp simulators were used containing basic solid-phase macrocomponents and differing in the hydroxide-to-silicon oxide ratio (Table 2.1).

The following binding materials and sorption additives were used to prepare cement compounds:

- Portland cement PC 500-D0 (CEM I 42.5B).
- Slag Portland cement SPC 400 (CEM III 32.5).
- Bentonite clay M4T1K.
- Clinoptilolite (Kholinsky deposit, Siberia).
- Superplasticizer C-3.

A cemented pulp composition, a binder type, a cement-compound loading capacity, and a water-to-binder ratio (W/B) were varied in the course of the research. The cement compound samples, $2 \times 2 \times 2$ cm in size, were placed in a humid-air atmosphere for hardening.

A set of experiments using the real pulp samples has been conducted at the Central radiochemical-plant laboratory of MCC to check VNIINM's recommendations. To carry out these investigations, the pulp sample with a volume of about 2 l was taken from a storage tank. The sample represented an inhomogeneous mass of sintered particles stuck together. The density and humidity of the pulp were, respectively, 1.55 g/cm^3 and 51.3 %. With the W/B ratio ranging from 0.7 to 0.9, the degree of the compound filling with the pulp was 4.5 %, 9 %, and 40 %.

3 Experiment Results and Their Discussion

3.1 Laboratory Investigations

The results of some laboratory experiments are shown in Figs. 2.1, 2.2, 2.3, 2.4, and 2.5.

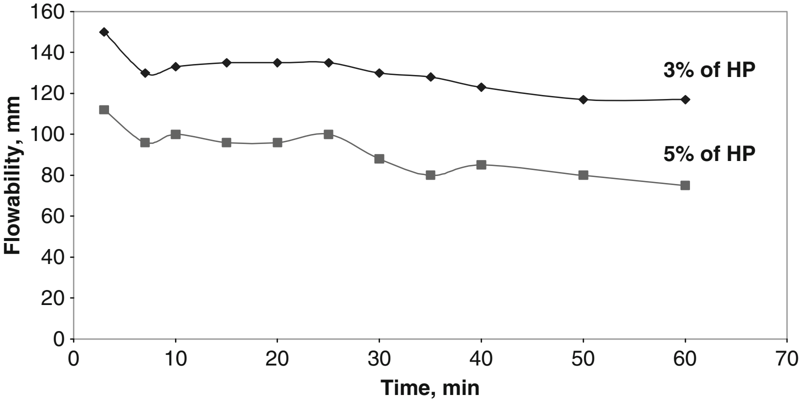

Fig. 2.1 Effect of loading capacity on cement paste flowability (simulated pulp)

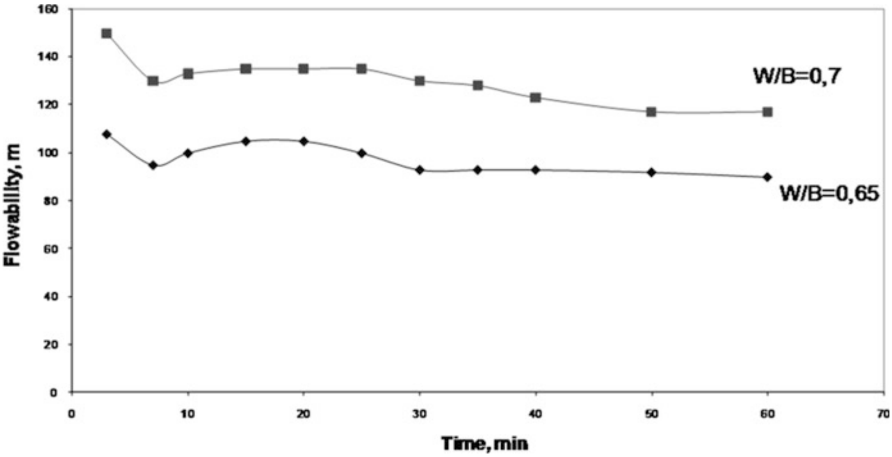

Fig. 2.2 Effect of water/binder ratio on cement paste flowability (simulated pulp)

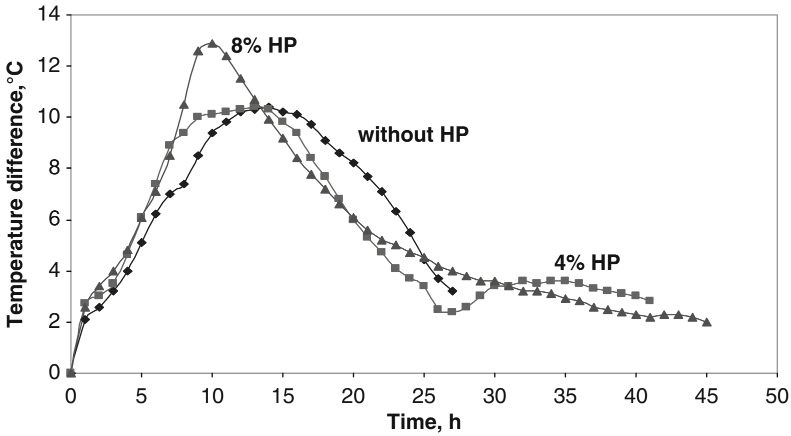

Fig. 2.3 Effect of pulp content in cement compound on heat generation (simulated pulp)

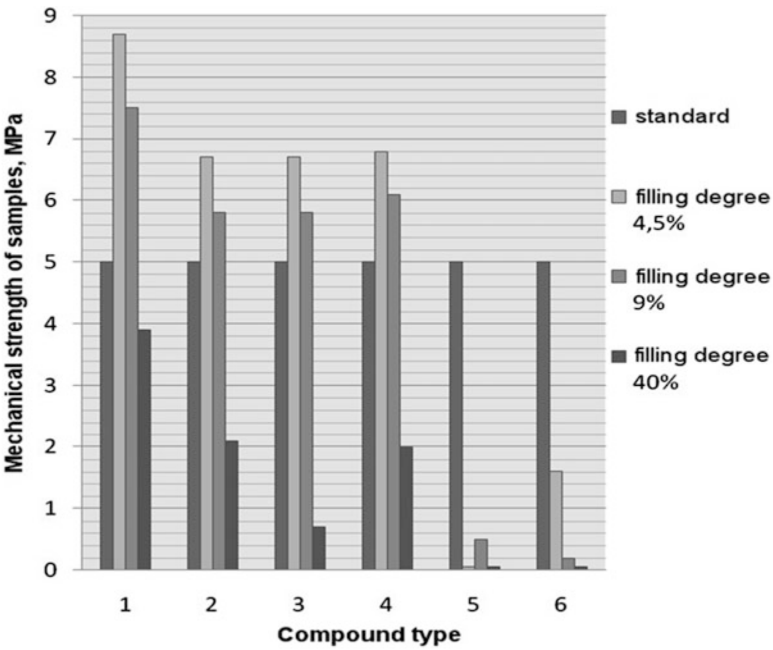

Fig. 2.4 Effect of loading capacity (filling degree) on mechanical strength of cement compound (real pulp from storage tank)

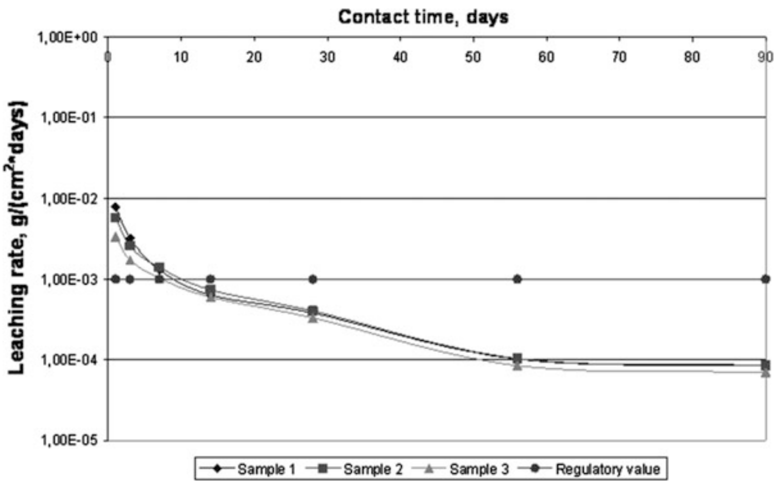

Fig. 2.5 Cesium-137 leaching tests for period 90 days (real pulp from storage tank)

Laboratory research results

- Portland cement and slag portland cement with sorbent additives (klinoptilolite or bentonite) may be used as a matrix material for MCC pulp immobilization.
- The cement compound had the required quality on mechanical stability, water resistance, freezing resistance, and leachability.
- Experiments helped to determine optimal parameters for cementation process and to make preliminary recommendations on technological regime of pulp cementation.

3.2 Testing of Pulse Mixer for Pulp Cementation

A.A. Bochvar Institute has developed the innovative cementation facility with a pulse mixer. The facility has the following advantages: there is no stirrer in it and cement compound is guaranteed to be discharged from the mixer. The testing objectives were to check (1) possibility to get homogeneous cement compound of a required quality and (2) preliminary technological recommendations made according to the laboratory research results.

Testing of pulse mixer description includes the following (Fig. 2.6). The cementation facility mixer was loaded with pulp simulators and a mixture of PC (or SPC) and bentonite (10 wt%), which was added to the mixer by permanent stirring for 20 min. Once completely loaded, the mixer was stirred for 5 min and then discharged. Samples were drawn in the beginning, in the middle and in the end of the discharge process to determine the flowability of the compound. The mechanical strength (after 7, 14, 28, 56, and 90 days), water resistance, freezing resistance, and leaching rate of the obtained cement compound were determined.

Pulse mixer testing showed

- Using the pulse mixer for pulp cementation makes it possible to produce a homogeneous cement compound with flowability allowing for the compound discharge from the mixer to the drum.
- The obtained cement compound had the required quality.

Based on results of the experiments, the recommendations have been provided on the cementation process parameters and characteristics of the cement compound obtained.

4 Conclusion

The obtained experimental data allowed to make preliminary technological recommendations on production of cement compounds that satisfy the national waste acceptance requirements.

The next step will be creation of full-scale pilot cementation facility and its testing using simulated pulp and real MCC pulp.

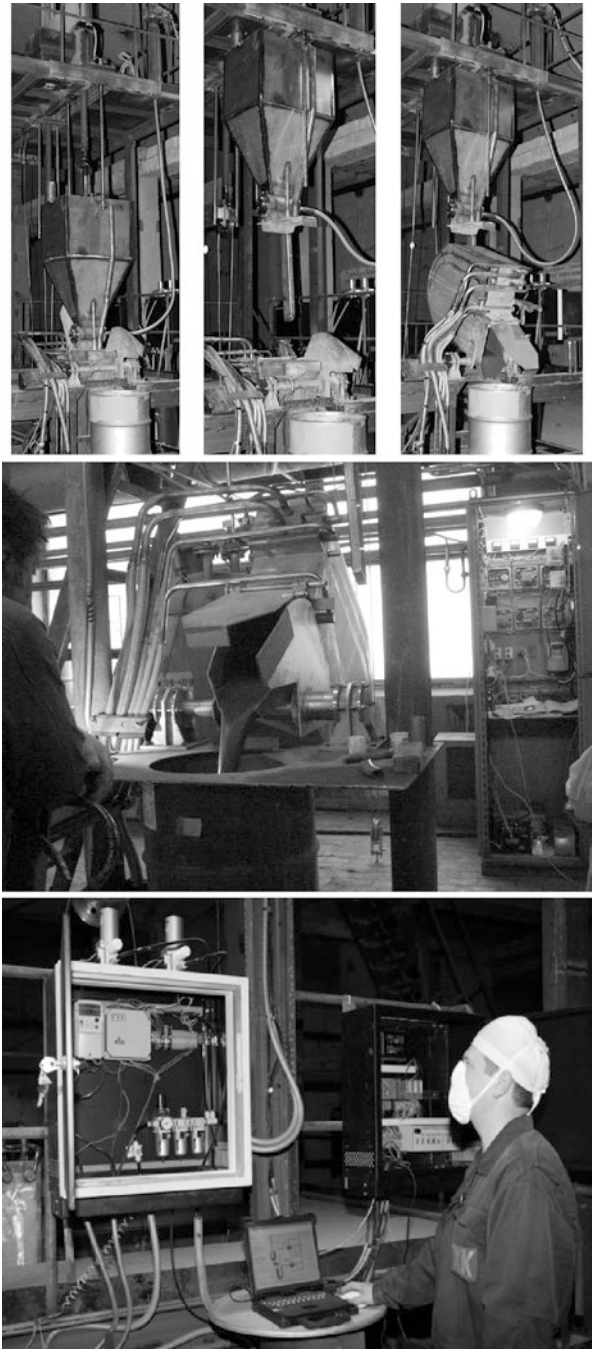

Fig. 2.6 Cementation pilot facility with pulse mixer

Springer

http://www.springer.com/978-1-4614-3444-3

Cement-Based Materials for Nuclear Waste Storage
Bart, F.; Cau-di-Coumes, C.; Frizon, F.; Lorente, S. (Eds.)
2013, XVIII, 266 p., Hardcover
ISBN: 978-1-4614-3444-3