Conditioning of Boron-Containing Low and Intermediate Level Liquid Radioactive Waste - 12041

Olga A. Gorbunova*, Tatiana S. Kamaeva**
* SUE SIA “Radon”, Moscow, Russia
** Vernadsky Institute of Geochemistry and Analytical Chemistry
Russian Academy of Sciences, Moscow, Russia

ABSTRACT

Improved cementation of low and intermediate level radioactive waste (ILW and LLW) aided by vortex electromagnetic treatment as well as silica addition was investigated. Positive effects including accelerated curing of boron-containing cement waste forms, improve end product quality, decreased product volume and reduced secondary LRW volume from equipment decontamination were established.

INTRODUCTION

Use of Nuclear power leads to formation and accumulation of large amounts of low and intermediate level liquid radioactive waste (LLRW and ILRW). Cementation is one of the most simple and effective ways of conditioning this type of radwaste.
It is common knowledge that boron-containing LRW from NPPs can be hard to solidify in cement. Cement cure happens in 14-56 days without special additives. Such waste forms type samples have very low strength and consequently insufficient fixation of radionuclides fixation within their structure.
Acid reaction of boron-containing LRW (pH 4…5) leads to neutralization of the cement alkaline minerals and prevents aquation. These two processes reduce the solidification rate of a cement product based on boron-containing LRW. . At the present time for this type of RW, alkaline additives (to neutralize boric acid) are commonly being used which increases end product volume, increases conditioning costs and operating costs.
As we have previously ascertained, cement solution treatment in a vortex electromagnetic field helps to accelerate solidification and to improve regulated properties of the cement product because of the intense mixing, mechanical and magnetic activation of the cement solution components. Ferromagnetic metal cores (length 2,5-3 cm, 0,5-0,7 in diameter) are being used as activating agents during vortex electromagnetic treatment . After passing through the mixing chamber, these particles are being separated and decontaminated for re-use.

EXPERIMENTAL METHOD

This research work is aimed at improving cementation technology of boron-containing LRW and its results can be applied at NPPs. The following results have been determined:
1) Accelerated curing of boron-containing cement products by means of vortex electromagnetic (physical) influence.
2) Optimization of vortex electromagnetic treatment (VET) using ferromagnetic particles in the form of fine powder (0,3-0,8 mm) or nano-particles (30-80 nm) of ferric oxides instead of ferromagnetic metal cores (length 2,5-3 cm, 0,5-0,7 in diameter).
3) Application of special additives which helps to increase speed of cement solidification and ^{137}Cs and ^{90}Sr radionuclides fixation (adsorption).

The treatment of solutions was carried out in laboratory vortex apparatus VA-100 (fig. 1). Vortex mixer VA-100 consists of inductor, where electrical windings are located which creates the intended rotating electromagnetic field. Inside the inductor there is a mixing chamber. Leak proof steel vessels, in which cement solution and ferromagnetic particles are loaded, are placed into the mixing chamber. Ferromagnetic particles under the influence of electromagnetic field start their rotation and forward motion, colliding and creating a vortex layer.

a) *b)* *c)*

Fig. 1. Vortex electromagnetic mixer: a) – mixing chamber construction: 1-vortex apparatus inductor; 2 – electrical windings; 3 – mixing chamber; 4 – ferromagnetic particles; 5 – spacing grating; b) – mixing chamber and control panel ; c) – erected and dismantled view of leak proof steel glass, ferromagnetic particles.

Samples of cement products from Portland cement and LRW (pH=5,03$^{\pm 0,05}$; solid residue 572,78$^{\pm 32,21}$ g/dm^3, suspended matter 118,00$^{\pm 6,00}$ g/dm^3, salt content 467,93$^{\pm 23,00}$ g/dm^3, among them borates 77,00$^{+6,00}$ g/dm^3; Σβ of Cs-137=1,4 · 10^7 Bq/dm) were prepared.
Boron-containing LRW was treated in a vortex electromagnetic field for 30, 60, 180 seconds before mixing with Portland cement. The following ferromagnetic particles for VET were used:
1- Metal cores (length 2,5-3cm, 0,5- 0,7 cm in diameter);
2- Fine powder of iron ferric oxide pigment Fe_2O_3, mean participle size 0,8 mm;
3- Nano-particles of ferric oxides Fe_2O_3 and Fe_3O_8 mean participle size 30-50nm.

LRW properties before and after VET were investigated by infrared spectrometry with the help of IR Fourier-transform spectrophotometer *640-FTIR (Varian, США)*, ZnSe base, resolution 2 cm^{-1}, attachment of disturbance of full internal reflection (*Pike MIRacle™, США*).
Structure of solidified cement product based on boron-containing LRW with ferromagnetic nano-particles was investigated with the help of scanning electronic microscope (SEM) *TESLA BS340 (Japan)*.
Several experiments examined the effect of the following strengthening and absorbing additives used: diatomite (1D), silica flour (2S), biosilica (2B), complex cement additive *Denka Super Cement® (Japan)* (2DSC) in amounts of 3, 5 and 10 % by weight.
The compressive strength of solidified boron-containing cement products after 7, 14, 28, 56 days and leaching rate of ^{137}Cs after 28 days was determined by standard technique.

RESULTS AND DISCUSSION

It was established that vortex electromagnetic treatment changes the state of boron-containing LRW. Fig.2 shows, that IR spectrums of LRW before and after 180 seconds of VET do not coincide. The 3640 cm^{-1} and 920 cm^{-1} peaks vanished. The 3640 cm^{-1} oscillation corresponds to valence oscillation of uncombined solitary (terminal) O-H bond, and 920 cm^{-1} oscillation corresponds to deformation oscillation A-O-H (where A is the scaffold atom, in this case, probably, boron or oxygen). Consequently, during the treatment of LRW, -O-H bond vanished. This broken bond yielded an acid medium of LRW, and slowed the cement solution cure for boron-containing LRW. Moreover, peaks in the range from 1450 cm^{-1} to 750 cm^{-1} changed. This indicates the boron product forms are changed in LRW.
From these results it was decided to treat only the liquid phase of the cement solution (LRW). This simplifies the process and increases its productivity and decreases energy usage at the expense of operation time decrease.
During the research of the vortex electromagnetic treatment parameters the treatment time (10, 30, 60, 180 sec), the type and amount of the activating agent (separable ferromagnetic particles or fine powder) and the solution composition (liquid phase only or whole cement solution) were all varied. As a result of this research work the following method of the VET was chosen: liquid phase of the cement solution with 3-5% by mass of fine-dispersed powder and nano-powder of ferric oxides treated in vortex mixer for 60 seconds, then mix the liquid phase including powders with cement. Some of the results are shown in table 1.

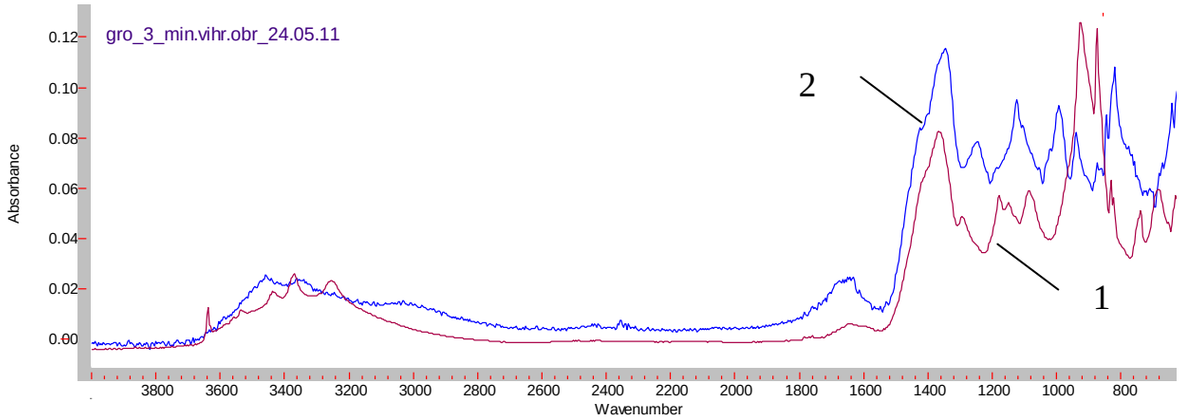

Fig. 2. IR spectrums of samples of boron-containing LRW: 1- before treatment (red); 2- after 3 min treatment (blue)

The results corroborate that VET increases the strength of the cement product almost in 1.2 – 1.5 times, increases frost-resistance, and therefore may improve Cs-137 and Sr-90 fixing in the cement matrix at the expense of its microstructure compacting.
The changes in the LRW by VET have positive effect on the curing and solidification of cemented LRW: time of the cement product curing decreased, strength increased evenly, samples obtained strength of 5MPa in 28 days.

Table I. *Properties of cement products based on boron-containing LRW, prepared with water-cement ratio* W/C=0,6 with the help of VET

VET conditions			Mortar spread ability, mm	Setting time, days	Compression strength, MPa				
Time, seconds	Solution composition[a)]	Type[b)] of activator-participle			7 days	14 days	28 days	56 days	After 30 cycles of freezing-thawing -40…+40^{0}C
Water									
Without VET			200	1	8,4	12,2	18,3	19,4	10,0
60	(1)	(3)	180	1	10,4	14,5	21,0	20,5	21,7
60		(4)	175	1	16,7	19,8	25,3[c)]	29,3	23,6
Boron-containing LRW									
Without VET			190	> 56	-	-	-	-	-[d)]
60	(1)	(3)	180	49	-	-	-	28,5	-
60	(2)		180	13-25	-	0,7	12,0	12,4	-
180			**145**	**2**	**4,3**	**15,9**	**16,7**	**20,2**	**-**
60		(4)	160	9-20	-	0,9	5,0	5,3	-
60		(5)	150	5-14	0,6	1,0	5,5	5,8	-

a) – **samples which were subjected to VET:** (1)- all the solution; (2)- only the liquid phase
b) – **ferromagnetic particles used:** (3) – metal cores 2,5-3 cm length;
(4) – fine powder of iron ferric oxide pigment Fe_2O_3, mean participle size 0,3-0,8 mm;
(5) – nano-particles of ferric oxides Fe_2O_3 and Fe_3O_8 mean participle size 30-50 nm
c) – sample investigated with the help of SEM (fig.3)
d) – was not determined

In case of cementation with VET solidification dynamics varies depending on activator-particle used. The use of Fe_2O_3 powder instead of separable ferromagnetic particles accelerates cement curing from 13 to 5-9 days. The use of nano-particles 30-80 nm size provides the best results for boron-containing LRW cementation with 60 seconds of VET. In this case, cement curing occurs in 5 days with equal strength development.
Pilot testing showed that large ferromagnetic metal cores obstruct the grating impeding the discharge of the radioactive cement mixture. This would require additional dangerous technological steps for their separation and decontamination as well as would increase volume of secondary waste because of their formation from mixer sluice out operation. It was determined that VET with Fe_2O_3 powders and nano-participles can simplify the process.

Hypothetically, Fe_2O_3 fine powder and nano-particles can reinforce micro-components increasing strength or take part in the growth of hydrated cement minerals which are responsible for early strength – calcium hydroaluminates and hydroalumoferrites. Solidified cement product microstructure character (composition "Portland cement + water + 3% mass of Fe_2O_3 fine powder") with preliminary VET for 60 sec confirms fine powder ferric oxides particles participation in formation of regular crystal structures in the solidified cement matrix (fig. 3).
It was established that use of strengthen and absorbing additives is required for receiving of final cement products with boron-containing LRW without VET. The investigation of modern additives from the construction industry showed accelerated curing of boron-containing solutions (Table II) with good results for Cs-137 leaching rates (fig.4) can be obtained without increasing the solidified waste volume.

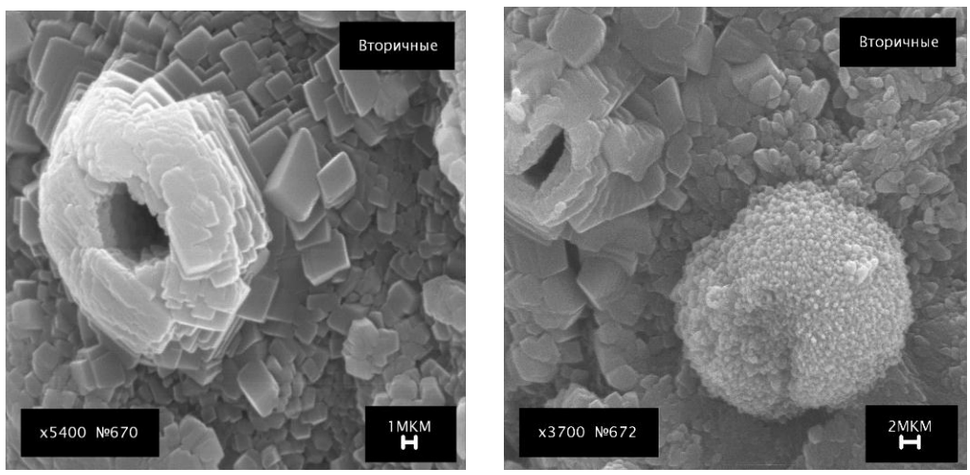

Fig. 3. Cement products microstructure with VET treated after 28 days of setting (60 sec, activating agent – fine powder of Fe_2O_3)

Table II. Influence of silica addition upon cement products based on boron-containing LRW properties (samples with water-cement ratio W/C=0,6)

Additive type	Setting time, hours-min	Compressive strength, MPa			Cs-137 leaching rate after 14-28 days of testing, g/cm^2·day
		7 days	28 days	56 days	
1D	0-51	13.48	15.01	28.40	$2{,}20\text{-}3{,}00 \cdot 10^{-4}$
2S	1-19	9,13	10,11	29,62	$2{,}55\text{-}3{,}05 \cdot 10^{-3}$
3B	1-13	17,83	19,19	30,96	$1{,}03\text{-}1{,}22 \cdot 10^{-3}$
2DSC	1-08	16,27	17,15	32,07	$3{,}37\text{-}3{,}88 \cdot 10^{-3}$

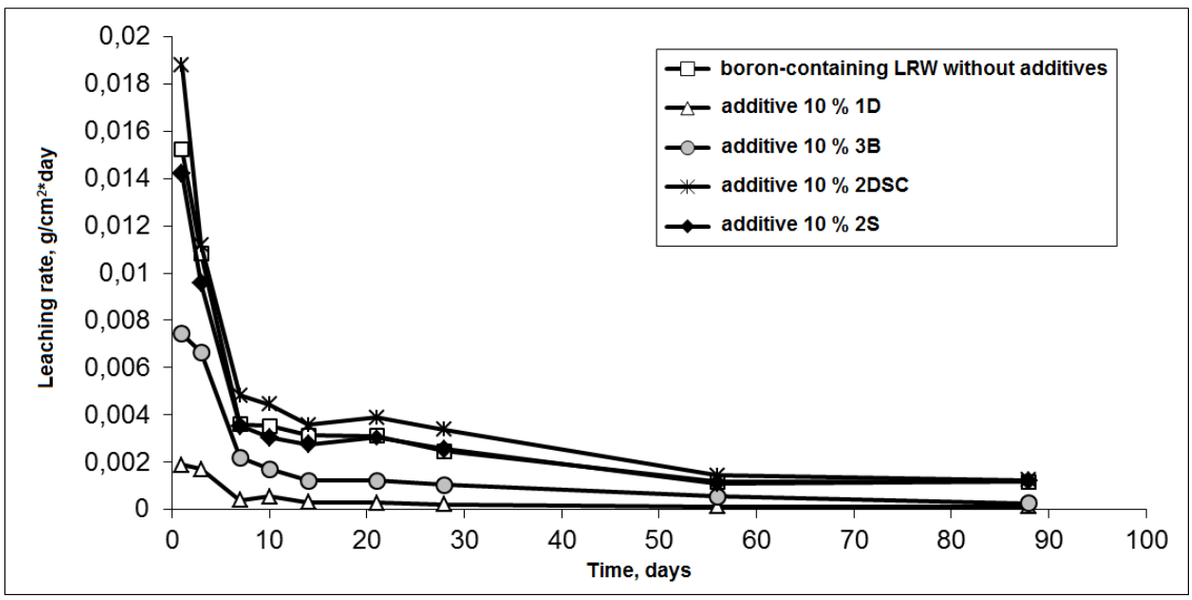

Fig. 4. Leaching rate of Cs-137 from cement products based on boron-containing LRW

CONCLUSIONS

These results established the possibility of boron-containing LRW cementation without the use of neutralizing alkaline additives that greatly increase the volume of the final product intended for long-term storage (burial). Physical (electromagnetic) treatment in a vortex mixer can change the state of LRW versus chemical treatment. By treating the liquid phase of cement solution only, instead of the whole solution, and using fine powder and nano-particles of ferric oxides instead of separable ferromagnetic cores for the activating agents the positive effect are obtained. VET for 1 to 3 minutes yields boron-containing LRW cemented products of satisfactory quality.
Silica addition at 10 % by weight will accelerate curing and solidification and to decrease radionuclide leaching rates from boron-containing cement products.

REFERENCES

1. Varlakov A.P., Gorbunova O.A., Fedorova O.V. et al., “Influence of Magnetic Field on Properties of Cement Product on the Base of Boron-Containing LRW”, WM’03 Conference, Tucson, AZ, USA (2003).
2. Olga Gorbunova, Alexandr Bariniv, Andrey Sobolev and Ivan Tananaev, “The Use of Nano-particles of Iron Oxide for Activation of Boron-Containing LRW during Cementation with Vortex Electromagnetic Processing”, “RADIOCHEMISTRY’09”, Moscow, pp. 298-300 (2009).
3. Gorbunova O.A., Kamaeva T.S. and Vasiliev E.V., “The Use of Nano-particles of Iron Oxide during Cementation of LRW with Vortex Electromagnetic Processing”, Scientific and Technical Magazine “Bulletin of Moscow State Building University” (“Vestnik MGSU”, http://www.mgsu.ru), № 5, 2011, pp. 208-213.