WM'00 Conference, February 27 – March 2, 2000, Tucson, AZ

PROPERTIES OF STONE CASTING AS A MATERIAL OF FACILITIES AND ITEMS IN RADIOACTIVE WASTE MANAGEMENT

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ABSTRACT

The effects of γ-radiation and high temperatures on stone casting (from pyroxenic porphyrite, gabbro diabase, halleflinta, pegmatite and so on) as a material of facilities and items in radioactive waste management were studied. It was found that γ-radiation (even at dose of 200 MGy) has a very small effect on properties (strength, microhardness, porosity and so on) and structure of the material. Simultaneous action of irradiation and temperatures of 600-750^{0}C have a higher effect on the properties and structure.

INTRODUCTION

The items from stone casting for radioactive wastes and their components are new ones. They are characterized by high corrosion, chemical and radiation stability, low penetrability, compatibility with rocks and so on. The material is good-moulded one. This feature gives rise a possibility to produce the items of the complicated shape via simple technology. It is comparatively cheap (for example, in comparison with metals).

Therefore, the items from stone casting can be used in radioactive waste management (at stages of treatment and packing, storage (especially in the case of long-term one), transportation and disposal to underground repositories. Stone casting can be utilized as constructional material upon creation of some units of repositories, tanks, capsules, artificial shielding barriers and special containers.

We have studied thermal, chemical and radiation stability of stone casting, the effects of irradiation and heating on its various properties and structure. The present report summarizes the data obtained.

EXPERIMENTAL

Three compositions of stone casting were studied. The composition I was prepared from a charge consisting of pyroxenic porphyrite (70% by weight), gabbro diabase (~30%) and chromite (~3%). The composition II consists of pyroxenic porphyrite and chromite (1-1.5%). Sitall and glass plastics were investigated. Composition III is stone casting and glass from halleflinta with additions of marble, magnesite and chromite.

The chemical composition of the studied stone castings is shown in Table 1. The properties of these castings are listed in Table 2.

Table 1. Chemical composition of stone casting (% by weight)

Composition number	Oxide	Content	Oxide	Content
I	SiO_2	50.50	TiO_2	2.16
I	Al_2O_3	12.52	Fe_2O	7.95
I	FeO	7.33	MnO	0.22
I	MgO	6.85	CaO	7.99
I	Na_2O	2.73	K_2O	0.86
I	Cr_2O_3	0.58	H_2O	0.04
I	Non-identified impurities	0.28	Sum	99.52
II	SiO_2	51.86	TiO_2	1.59
II	Al_2O_3	13.40	Fe_2O	3.55
II	FeO	7.33	MnO	0.18
II	MgO	8.27	CaO	9.67
II	Na_2O	2.23	K_2O	0.80
II	Cr_2O_3	0.38	H_2O	0.05
II	Non-identified impurities	0.34	Sum	99.65
III	SiO_2	53.13	TiO_2	0.08
III	Al_2O_3	12.70	Fe_2O	1.37
III	FeO	0.72	MnO	0.045
III	MgO	8.92	CaO	16.10
III	Na_2O	4.27	K_2O	0.66
III	Cr_2O_3	0.78	H_2O	0.11
III	Non-identified impurities	0.61	Sum	99.57

Table 2. Properties of stone casting

Property	Composition I	Composition II	Composition III
Three-point bending strength, MPa	800	1020	770
Specific impact viscosity, kg cm^{-1}	3.5	3.3	3.0
Stability to action of 20% HCl solution, %	95	99.8	99.09

In laboratory, charges were melted in silite furnace under oxidative conditions in corundum crucibles (volume 0.5 dm^3) at 1350^0C, melts were inserted to heated ground mould, crystallized for 30 min at 900-950^0C, then cooled for 15-17 h. Samples of stone casting produced in the factory was also studied.

Upon modelling of thermoradiation processes taking place upon storage of high-level radioactive wastes, we proposed that maximal temperatures are not over 600-750^0C and maximal radiation dose is 100 MGy. For irradiation, three ^{60}Co γ-ray sources with maximal dose rates 52, 60 and 100 kGy h^{-1} were used.

The changes of phase composition, structure, microhardness, three-point bending strength, valent state of iron, water absorption, porosity and so on as a result of irradiation and heating were measured. For determinations, diffractometer, electron microscope, microhardness gauge, ESR and Moessbauer spectrometers were used.

RESULTS AND DISCUSSION

Stone castings of all three compositions have no cavities. Porosity of stone castings of compositions II and III are equal to 0.1 and 0.7%, respectively. Water absorptions for these materials are equal to 0.08 and 0.2%, respectively. However, the growth of pyroxene content leads to the increase in porosity and water absorption.

The changes of microhardness at room temperature in a dependence on absorbed dose are similar for all three compositions (see Fig.1). With increasing dose, microhardness decreases by 15-30% at doses to 20 MGy, then it goes to plateau. At dose 200 MGy, microhardness of compositions I and II approaches the initial value. The highest change of microporosity was observed for glass of composition II and the lowest change - for composition III.

Figure 2 shows the dependencies of three-point bending strength on time of thermotreatment at 750^0C. It is seen that at initial stages of heating (to 100 h), the sharp decrease in strength for all three compositions takes place. At further heating, the values of strength are stabilized. The lowest change is observed for composition III.

In connection with the differences in chemical composition (see Table 1), the studied samples of stone casting have the different microstructure. However, the differences in microstructure between the initial and irradiated samples were almost not observed. Upon long-term heating, the formation of dust at some parts of the samples takes place. The reason is crystallization of residual glass.

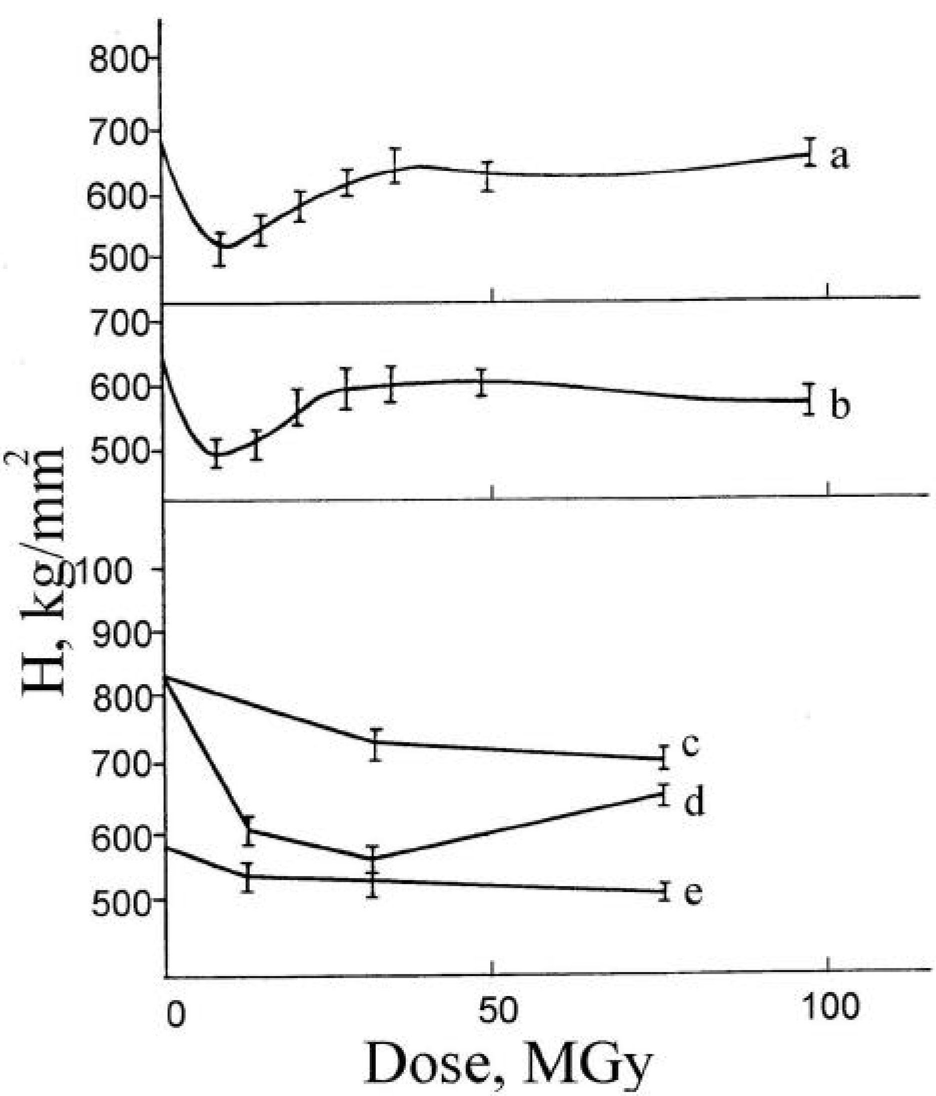

Fig. 1. Dependence of microhardness H on radiation dose: *a* – casting of composition I; *b* – casting of composition II (tube); *c* – sitall of composition II; *d* – glass of composition II; *e* – casting of composition III.

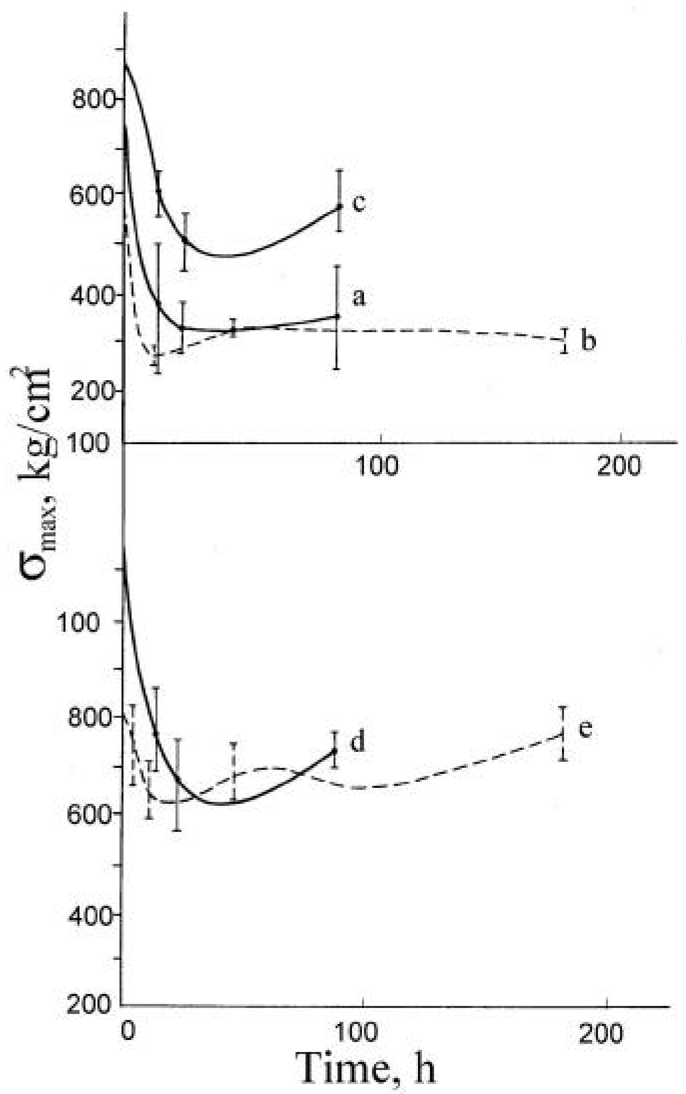

Fig.2. Variation of three-point bending strength (σ_{max}) of rocks and stone castings on time of thermotreatment at 750°C: *a* – pyroxenic porphyrite; *b* – gabbro diabase; *c* – casting of composition I (plate); *d, e* – casting of composition II (tube).

X-Ray phase analysis showed that the noticeable phase conversions in monolithic sample of composition I were not occurred upon irradiation and heating. However, heating of the powder at 750^0C led to the disappearance of magnetite maximums and to the appearance of hematite maximums. It means that oxidation of powder at the sample surface proceeds under these conditions. The phase conversions of the material of composition II were not noted upon irradiation and heating (independent of the sample state). Upon irradiation of stone casting and glass of composition III, the changes in structure were not found. However, heating gave rise to dust-like inclusions.

In order to determine the content of Fe^{2+} and Fe^{3+} ions in stone casting, ESR and Moessbauer methods were used. In the case of the sample of composition III and porphyrite casting, ESR spectra are wide singlets with g-factor ~2.01 and $\Delta H_{1/2}$ = 70 mT. They belong to Fe^{3+} ions. The concentrations of Fe^{3+} ions for casting from halleflinta are the same for the initial, irradiated and heated samples. The same situation is observed for the initial and irradiated samples of casting from porphyrite. However, in thermotreated (for 105 days at 750^0C) sample, the concentration of Fe^{3+} increased by 2 orders of magnitude. In the case of casting of composition I, ESR spectra show the presence of ferromagnetic phase Fe_3O_4. The comparison of ESR data with the results on phase state shows that γ-irradiation does not change the valent state of iron. Upon thermotreatment of monolithic samples, the considerable changes in iron oxidation state are also not observed. The oxidation of ironic minerals occurs only in the surface layers of the samples. This leads to the increase in Fe^{3+} concentration. The changes are not observed in stone casting from halleflinta containing a small amount of iron (almost all iron in it is present in three-valent state).

As mentioned, Moessbauer spectroscopy was also used for determination of iron concentrations. It was obtained that in rocks (porphyrite, diabase) Fe^{2+} ions prevail; Fe^{3+} ions with octahedral neighborhood (in silicate composition) and Fe_2O_3 (in diabase) are also observed. After heating of powder samples of rocks at 750^0C, oxidation of Fe^{2+} into Fe^{3+} takes place, the Fe_2O_3 concentration in diabase being increased. Irradiation does not result in a noticeable changes in Moessbauer spectra of the samples.

In the spectra of casting of composition I, mainly Fe^{2+} ions and Fe_3O_4, as well as small concentrations of Fe^{3+} ions with octahedral neighborhood are observed. In the spectra of irradiated samples, no new isomer shifts are seen indicating to a change in valent state of iron.

Heating to 750^0C results in formation of Fe^{3+} with octahedral neighborhood and Fe_2O_3. Comparison of Moessbauer spectra of initial samples of porphyrite casting, sitall and glass makes it possible to conclude that crystallinity degree has a small effect on oxidation state of iron ions, isomer shifts indicating to the presence of Fe^{2+} ions with impurity of Fe^{3+} ions. However, the width of absorption band being characteristic of symmetry of nearest neighborhood of iron ions, is less for sitalls than for porphyrite casting and glass.

In the spectra of all heat-treated samples, isomer shifts are observed indicating to the presence of Fe^{3+} with octahedral neighborhood. Irradiation virtually does not change Moessbauer spectra of the samples.

CONCLUSION

The obtained data allow us to draw the following conclusion:

1. γ-Irradiation (up to dose 100 MGy) and long-term thermotreatment of stone casting at 750°C does not lead to a considerable change in phase composition and structure. At thermotreatment, a small crystallization of residual glass phase is only observed.

2. γ-Irradiation virtually does not change the valent state of iron ions. Thermotreatment of stone casting containing a noticeable amount of iron at 750°C gives rise to somewhat increase in Fe^{3+} concentration. In casting on the base of halleflinta in which almost all iron is present in three-valent state, no changes take place.

3. At initial stages of irradiation (to dose 20 MGy), there is a decrease in strength parameters by 10-30%; at further irradiation, they approach the initial values. The effect of thermotreatment is somewhat higher.

4. The studied types of stone casting have high radiation, thermal and chemical stability, and they can be used as a material in radioactive waste management.