

MATRIXES FOR IMMOBILIZATION OF THE RADIOACTIVE WASTE AND COMPARATIVE ANALYSIS THEIR PHYSICOCHEMICAL AND TECHNICAL CHARACTERISTICS

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ABSTRACT

The problem of the immobilization of the radioactive waste is one of the important problems for the nuclear industry and all mankind's. The most reliable method is the inclusion of waste in glassy or mineral-like matrix. The process of the vitrifying of the radioactive waste is composite owing to high requirements shown to matrixes and to process of the vitrifying of waste.

Matrixes with the included radioactive waste should be chemically, thermally and radiation stable. Processes of their vitrifying should be reliable, technically simple, as they carried out at distance control. Different glassy and mineral-like systems and technical possibilities of the radioactive waste vitrifying processes realizing are briefly reviewed in the given report.

In the beginning the glassy system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$, having some technological advantage: low melting point, capability liquid fluxing by the phosphoric acid, was studied. The range of the vitrifying in this system at different temperature is shown in Fig. 1.

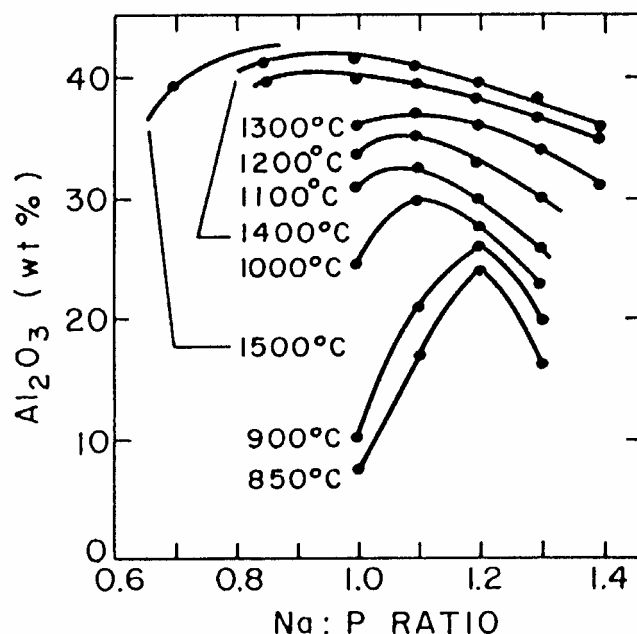


Fig. 1 Inclusion of the Al_2O_3 in glasses in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ as a function of the Molar Ratio Na : P and melting point.

From the given data it is visible, that the contents of Al_2O_3 in glass can reach 20-40 % wt. at the temperature variation from 900°C up to 1400°C . And if to use this system for sodium – aluminum-containing waste, the contents of the calcinated waste in glass can reach 40-55 % wt. the leaching rate of this system in water was investigated at 20°C . The data are given in Table I.

Table I Leaching Rate of Na-Al-Phosphate Glasses in Water

| Composition, %, wt. | | | Leaching rate at 20°C , $\text{g}/\text{cm}^2 \text{ day} \times 10^{-5}$ |
|-----------------------|-------------------------|------------------------|---|
| Na_2O | Al_2O_3 | P_2O_5 | |
| 25.4 | 26.0 | 48.6 | 0.2 |
| 30.1 | 31.0 | 38.9 | 0.29 |
| 28.2 | 34.0 | 37.2 | 0.26 |
| 28.4 | 35.0 | 36.6 | 0.84 |
| 27.5 | 37.0 | 35.5 | 0.23 |
| 26.6 | 39.0 | 34.4 | 1.18 |
| 25.8 | 41.0 | 33.2 | 1.10 |

Apparently, that the leaching rate of the matrix in water ($\sim 10^{-5}$ - 10^{-6} $\text{g}/\text{cm}^2 \text{ day}$) satisfies to the requirements, shown to materials for the burial of radioactive waste. Besides it was showed, that many elements from waste are well included into these glasses, namely, chromium, iron, nickel, Ca, etc.

Glassy matrix on the basis of the given system are introduction on firm PA "MAYAK", where the shop of the vitrifying of high level radioactive waste (EF-500/1p) was built, which one works already many years.

However phosphate glasses have essential lacks: 1. The range of the optimal glasses is rather narrow and either the leaching rate or the temperature of cooking can significantly increased at the glass composition change; 2. Some elements inclusive in waste (for example, Fe, Cr ...) increase the degree of the glassy matrixes crystallization.

The boron-phosphate and fluorine- phosphate glassy systems were studied also. Usage of the boron-phosphate glasses some improved situation, but it does not change the business essentially. Usage of the fluorine-phosphate system $\text{Na}_2\text{O}-(\text{Al}_2\text{O}_3+\text{MeF}_3$, where $\text{Me} = \text{Al, Fe, Cr}$ etc.)- P_2O_5 gives some advantages: the melting temperature is decreased; stone-like crystalline melts possessing high chemical stability in water at 20°C - (10^{-6} - 10^{-7} $\text{g}/\text{cm}^2 \text{ day}$) inclusive up to 45-50 % wt. of the sum of waste are obtained. These melts are crystallized and they do not change their phase composition and chemical stability in water over a long period of time at 300 - 500°C , thus the composition of waste can vary in rather broad limits. The luck of the system is high aggressiveness of fluorine-phosphate melt.

The system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}-\text{B}_2\text{O}_3-\text{SiO}_2$ was investigated also. The range of first sections glass system is shown in the fig. 2. It is visible from represented data, that in the given system quantity of inclusive waste is 32-38 % wt. in dependence on glasses cooking temperature, i.e. nearly the same, as in sodium-aluminum-phosphate system. However the glasses cooking temperature of this system is a little bit higher.

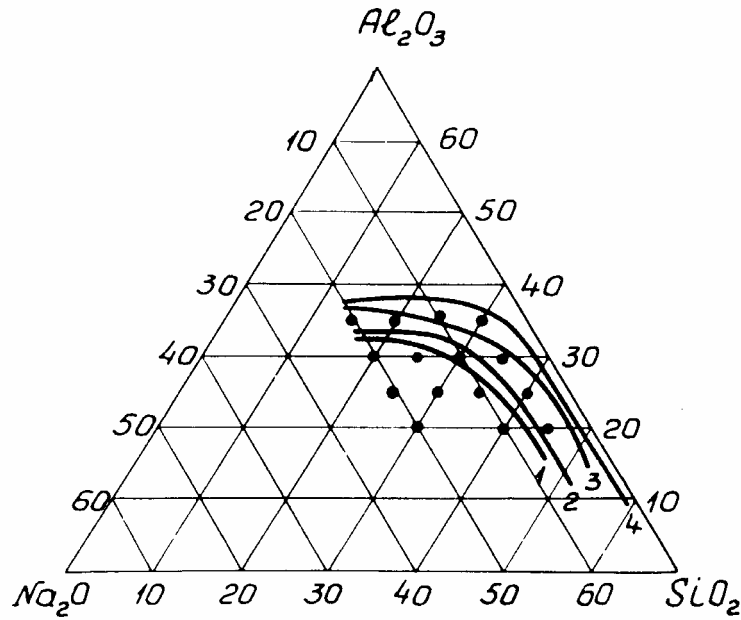


Fig. 2 Range of Glass in the System $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}-\text{B}_2\text{O}_3-\text{SiO}_2$, with $\text{CaO}=15\%$ wt., $\text{B}_2\text{O}_3=15\%$ wt. Melting Temperature: 1=1100, 2=1200, 3=1300, 4=1400 $^\circ\text{C}$.

The leaching rate of glasses of this system, determined from sodium leaching, is shown in Table II. The leaching rate of glasses of this system is a little bit better, than for the phosphate system, but main, that the leaching rate of glasses depends on glass composition much less. Essential lack of this boron - silicate glasses is the poor fixation of some elements inclusive in waste, such as Cr or Mo, which one in presence of Na will forms a separate water soluble phase of sodium chromates or molybdates. Lack of these glasses is also heightened crystallization at the large contents of some elements (for example, such as Ca).

Table II Leaching rate of glasses in water at 20 $^\circ\text{C}$ in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}-\text{B}_2\text{O}_3-\text{SiO}_2$

| Composition, %, wt. | | | | | Leaching rate, $\text{g}/\text{cm}^2 \text{ day} \times 10^{-6}$ |
|-----------------------|-------------------------|--------------|------------------------|----------------|--|
| Na_2O | Al_2O_3 | CaO | B_2O_3 | SiO_2 | |
| 20 | 20 | 0 | 10 | 50 | 9.3 |
| 25 | 20 | 0 | 10 | 45 | 11.7 |
| 20 | 15 | 0 | 10 | 55 | 5.7 |
| 20 | 15 | 0 | 20 | 45 | 0.9 |
| 30 | 15 | 0 | 20 | 35 | 7.1 |
| 40 | 20 | 0 | 5 | 35 | 47.0 |
| 20 | 30 | 10 | 15 | 25 | 1.7 |
| 20 | 20 | 10 | 15 | 35 | 5.0 |
| 10 | 30 | 15 | 15 | 30 | 0.2 |
| 10 | 20 | 15 | 15 | 40 | 0.1 |
| 20 | 30 | 15 | 15 | 20 | 13.0 |
| 20 | 20 | 15 | 15 | 30 | 18.0 |

Both sodium–aluminum-phosphate and sodium–aluminum-boron-silicate glassy matrixes are suitable for burial of some kind of the radioactive waste. However for α -active waste with a large half-life of high level of activity it is desirable to have matrixes with smaller leaching rate. Basalt-like matrix and matrix on the basis of the stone casting from some rocks were offered for obtaining the materials with smaller leaching rate.

The conducted investigation on inclusion of different solid radioactive waste (SRW) components and liquid highly active waste (HAW), mainly of actinides, in a structure of a number of rocks, has resulted in conclusion, that the basalt-like matrix on the basis of the stone casting is the most perspective system for these purposes. It represents a melted mixture consisting from porphirite, modified by 1.5 % wt. of ferrum chromite - $\text{Fe}^{+2} \text{Cr}_2\text{O}_4$, with adding 10-20 % wt. of the boric anhydride. Stone casting is more uniformly and practically without gases. This is its advantages in comparison with initial rocks. The applying a boric anhydride as the adding is effective for all investigated compositions inclusive uranium, thorium, strontium, cesium, REE and plutonium. Thus, the tendered system is universal enough and allows to obtain the homogeneous melts (glasses) at the temperatures not more than 1250°C .

The indicated matrix on the basis of the stone casting is capable to include in the structure rather large quantity of radioelements oxides for the purposes of the immobilization (tens % wt.) – main radionuclides SRW and HAW, obtained at processing of the spent nuclear fuel. It is necessary to mark, that this matrix can include not less 15-20 % wt. of plutonium dioxide. The experimentally determined leaching rate of the sum of matrix components in ultra clean deionized water at 20°C is $(0.5 - 5) \cdot 10^{-7} \text{ g/cm}^2 \text{ day}$ in depending on nature of inclusive element and on its contents in the matrix (Table III).

Table III Composition and leaching rate of melts in deionized water at 20°C(x10⁻⁷ g/cm² day) (SC – Stone Casting).

| Component | Composition % wt. | | | Leaching rate | Composition % wt. | | Leaching rate |
|--------------------------------|-------------------|-------------------------------|-------|---------------|-------------------|-------|---------------|
| | SC | B ₂ O ₃ | Oxide | | SC | Oxide | |
| U ₃ O ₈ | 75 | 8 | 17 | 0.5 | 81 | 19 | 2.5 |
| | 71 | 7 | 22 | 2.0 | 77 | 23 | 2.0 |
| | 72 | 11 | 17 | 1.0 | - | - | - |
| | 69 | 10 | 21 | 2.0 | - | - | - |
| ThO ₂ | 75 | 8 | 17 | 0.5 | 81 | 19 | 0.5 |
| | 71 | 7 | 22 | 0.5 | 77 | 23 | 0.5 |
| | 72 | 11 | 17 | 0.5 | - | - | - |
| | 69 | 10 | 21 | 0.5 | - | - | - |
| SrO | 77 | 8 | 15 | 2.5 | - | - | - |
| | 74 | 11 | 15 | 1.5 | - | - | - |
| Cs ₂ O | 77 | 8 | 15 | 0.5 | - | - | - |
| | 71 | 7 | 22 | 0.5 | - | - | - |
| CeO ₂ | 77 | 8 | 15 | 2.0 | 91 | 9 | 0.5 |
| | 78 | 10 | 12 | 2.0 | 87 | 13 | 1.0 |
| | 76 | 9 | 15 | 2.0 | 83 | 17 | 0.5 |
| Nd ₂ O ₃ | 82 | 10 | 8 | 2.0 | 91 | 9 | 1.5 |
| | 78 | 10 | 12 | 2.0 | 87 | 13 | 1.5 |
| | 76 | 9 | 15 | 2.0 | 83 | 17 | 2.0 |
| PuO ₂ | 74 | 7 | 19 | 0.2 | 80 | 20 | 0.5 |
| | 71 | 11 | 18 | 0.2 | - | - | - |
| | 90 | 10 | - | 3.0 | 100 | - | 2.0 |

As to without boron basalt systems (Table III), their technological lack is higher melting temperature, resulting in obtaining of homogeneous stone-like melt or glasses. It is ~1400°C, and it is necessary to use the special equipment, for example, inductive smelter with a cold crucible (IFCC) in immobilization technology. It have been shown, that leaching rate in water at 20°C of without boron systems inclusive such components, as the U, Th, Cs, Nd, Pu oxides in quantities ~ 20 % wt. lies within the limits (0,5 - 1,5)*10⁻⁷ g/cm² day. They do not yield to systems with the adding of boron oxide on this parameter and, thus, they have quite reasonable operating characteristics. Leaching rate of materials in water little depends on nature and content of inclusive oxide and corresponds to value, determined for stone casting. These circumstances create the definite technological advantages, as the real contents of the indicated components in waste of a different genesis can notably differ, and it will little influence on the investigated without boron system.

In real conditions the absorbed doses of the self-irradiation alpha radioactive materials may be rather significant. In the present work it was 0.5 MGy/day at the introducing 20 % wt. of plutonium oxide in a matrix. Thus the investigation of influencing of this factor on the basic properties of boron and without boron systems inclusive plutonium seems to be rather important.

On the basis of a number of experiments and on exploitation experience of high activity materials in such articles, as radiation sources and radioactive heat sources, it is known, that the self-irradiation may lead to amorphisation of matter if its initial form was crystalline, and to the glass crystallization. Most obviously these processes take place in alpha radioactive materials. In matrixes including, for example, radioactive promethium, cesium, and strontium they also take place to a lesser degree. At all events, in the present work the crystallization of boron-basalt systems inclusive about 20 % wt. PuO_2 , and obtained as the glass, clearly takes place at absorbed doses about 100-200 MGy, i.e. after 200-400 days from the moment of manufacturing. The data of the conducted X-ray measurements testify to it. It causes the necessity of investigations of crystallization influencing on properties of materials including the different radioactive waste.

Dependence of leaching rate of plutonium on time in ultra pure deionised water is given in Fig. 3.

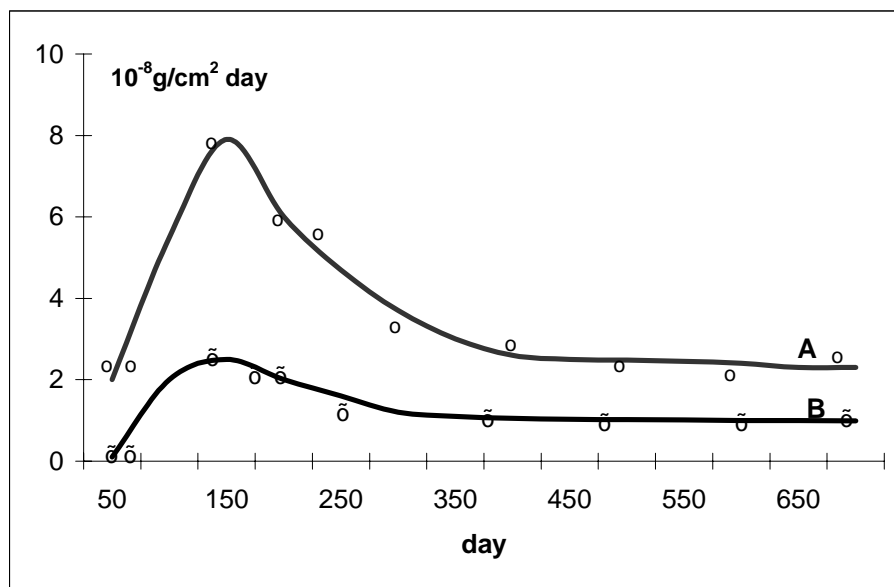


Fig. 3 Leaching Rate of the Boron-Basalt Matrixes Components Sum (A), and Leaching Rate of Plutonium (B), in Time Dependence (dose rate – 0.5 MGy/day).

From given data are visible, that the radiation crystallization has influence on values of leaching rate during time up to ~ 1 year from the moment of the material manufacturing, i.e. up to values of air doses about 150 MGy. Thus the process of phase transformations entails a minor decrease of chemical stability. The stability of materials to dissolution in water practically is reduced and does not vary in time after finishing of the radiation crystallization process. Thus self-irradiation has influence on the given property mainly during transformation of glassy matrix in crystalline. Influencing of the self-irradiation on chemical properties of crystalline samples, after approximately year from the moment of their manufacturing, is not marked.

It will be agreed with data obtained at investigation of the influencing of the self-irradiation on without boron crystalline matrixes. For these materials the self-irradiation does not have noticeable influencing both on leaching rate of the sum of elements, and on leaching rate of plutonium from them, and are, accordingly, $5-8 \cdot 10^{-8}$ and $2-4 \cdot 10^{-8} \text{ g/cm}^2 \text{ day}$.

Represented data concerned to boron-basalt and without boron systems inclusive the personal component of the radioactive waste. However, the studied materials and methods of their synthesizing can be applied to composite compositions of real manufacturing waste inclusive different as radioactive, so "cold" chemical components. With the purpose of check it, the researches on inclusion of mixtures of different components applicable to a number of real wastes of PA «Mayak» in boron-basalt matrix were conducted.

In this case at the contents of such complex waste, as HAW and SRW in boron-basalt matrix in quantity up to 40 % wt. homogeneous glassy or stone-like melts are obtained. The increase of inclusive waste quantity up to 60 % wt. is possible at absence in the mixture of such elements, difficulty joining in glass, as zirconium and chromium. The data of the investigation of the materials stability, inclusive different types of waste, to dissolution in water are listed in Table IV.

Table IV Leaching Rate of Materials in Ultra Pure Deionisated Water $\times 10^{-7}$ g/cm² day (on the Sum of Components) *)

| Naming of waste | Main components of waste | Waste contents, % wt. | Leaching rate, $\times 10^{-7}$ g/cm ² day | | | |
|------------------------|--------------------------|-----------------------|---|-----|-----|-----|
| | | | B ₂ O ₃ , % wt. | | | |
| | | | 0 | 8 | 12 | 20 |
| SRW, without graphite | Mg, Ca, Al, Fe | 20 | 3.5 | 1.0 | 1.0 | 1.0 |
| | | 40 | 10 | 5 | 5 | 10 |
| HAW, raphinate 1 cycle | Fe, Zr, Mo | 20 | | 1.0 | 1.0 | 1.0 |
| | | 40 | | 1.0 | 1.0 | 1.0 |
| HAW, fraction Sr, Cs | Ca, Ba | 20 | | 1.0 | 1.0 | 1.0 |
| | | 40 | | 1.5 | 1.0 | 1.0 |
| HAW, fraction TPE, REE | Zr, REE | 20 | | 0.7 | 1.0 | 1.0 |
| | | 40 | | 0.5 | 1.0 | 1.0 |
| HAW, raphinate 6 cycle | Al, Fe, Zr, Cr, Mo | 20 | | 2.0 | 3.0 | 1.5 |
| | | 40 | | 2.0 | 3.0 | 3.0 |

*) Basalt is the remainder.

Obtained data demonstrate, that the chemical stability of boron-basalt composition with the real waste of PA "Mayak" in quantity up to 40 % wt., are quite reasonable to their immobilization.

All represented and some other data are shown in the general Table V. The main properties of matrixes are shown and compared in it: waste inclusion degree, cooking or sintering (in case of

ceramics) temperature, leaching rate interval, applicability of matrixes for different fractions of the RAW from processing of SNF and conversion of weapon plutonium, applicability for process of the immobilization of different vehicles, advantages and lacks of matrixes and technological schemes, degree of matrixes study, readiness of processes. It is possible to make some conclusions:

1. Different glassy and mineral-like system as matrixes for the immobilization of RAW was investigated.
2. Matrixes with not enough low leaching rates - 10^{-5} - 10^{-6} g/cm² day are obtained in the technologically convenient processes of the immobilization of the RAW with usage of liquid fluxing by H₃PO₄ and low temperature of cooking.
3. The manufacturing technology of materials with enough low leaching rate - 10^{-7} - 10^{-8} g/cm² day is much more complex and it suppose the usage of rather high temperatures (1400-1800⁰C) and complicate, not enough reliable devices (for example, IFCC) or high temperature furnaces with heaters from MoSi₂, LaCrO₃.
4. On our view, it is necessary to work in the direction: 1 - decrease of the leaching rate of fusible matrixes; 2 - increase of the reliability and productivity degree of high temperature smelters; 3 - development of the one-time melting crucibles; 4 - development of the resistant construction materials for crucibles - smelters (one or reusable).
5. It is necessary to develop the methods of matrix quality control in view of complexity of obtained materials precise composition holding in radiochemical production.
6. Now in Russia sodium – aluminum - phosphate glassy matrixes have used for the RAW immobilization in radiochemical productions, however they should be exchanged on aluminum – boron - silicate or mineral-like matrix.

Table V Matrixes comparative characteristics *Notice. Leaching rate, g/cm²day,-(V₁)

| Matrixes (glassy and mineral-like) | | Matrixes properties | | | Technology | | | |
|------------------------------------|--|---------------------|-------------------------------|--|---|---|--|---|
| | | T manufactu ring °C | Inclusive waste content % wt. | *V ₁ , Initial crystalline matrix | Possible apparatus | Degree of technology investigation | Matrixes and technology preferences | Matrixes and technology lacks |
| 1 | Sodium-aluminum-phosphate (glass) | 900-1100 | 30-45 (IFCC-up to 50 % SRW) | $10^{-5} - 10^{-6}$ $10^{-4} - 10^{-3}$ | Ceramic smelter electro furnace EF-500/1p | Applied in PA «MAYAK» | Low T cooking, possibility of wet fluxing | High V ₁ , its strong dependence on composition, high crystallization at the presence of some elements |
| 2 | Sodium-aluminum-boron –phosphate (glass) | 850-1050 | 30-45 (IFCC-up to 50 % SRW) | $10^{-5} - 10^{-6}$ $10^{-4} - 10^{-3}$ | Electro furnace EF-500/1p | Applied in PA «MAYAK» | -----“”-----, less crystallization against phosphate glass | -----“”----- |
| 3 | Sodium-aluminum-ortho-phosphate (apatite-like) | 850-1000 | 40-50 | $10^{-6} - 10^{-7}$ $10^{-6} - 10^{-5}$ | Electro furnace EF-500/1p | Special difficulty at applying does not wait | Initial stone-like melts are crystalline, V ₁ are low , does not change and little depends on composition | High aggressive melt |
| 4 | Boron-silicate (glass) | 1100-1200 | 30-45 (IFCC-up to 50 % SRW) | $10^{-6} - 10^{-7}$ $n*10^{-6}$ | Electro furnace EF-500/1p | Special difficulty at applying does not wait | Lower V ₁ , and dependence on composition and crystallizing | High obtaining T, the wash of gas-pipe is difficult |
| 5 | Basalt-like | 1400 | ~30 | $10^{-7} - 10^{-8}$ $n*10^{-7}$ | IFCC | Insufficiently technology and apparatus development | Low V ₁ , dependence on crystallizing are absent | High synthesis T, complicate devises |
| 6 | Basalt-like + B ₂ O ₃ | 1200-1300 | ~30 | $10^{-7} - 10^{-8}$ $n*10^{-7}$ | EF-500/1p, IFCC, (hot pressing, cold pressing) | Insufficiently technology and apparatus development | Low V ₁ , Dependence on crystallizing are absent | Insufficiently technology and apparatus development |
| 7 | Chromite-niobate (mineral-like) | 1350-1450 | 30-40 | $10^{-7} - 10^{-9}$ $n*10^{-8}$ | Cold pressing and sintering in high temperature furnaces | It is developed in laboratory | Low V ₁ , Dependence on crystallizing is absent. | Poor technology development |
| 8 | Chromite-niobate + basalt (mineral-like) | 1000-1100 | 30-40 | $10^{-7} - 10^{-9}$ $n*10^{-7}$ | Cold pressing and sintering, hot pressing (it is possible to decrease T up to 700-800°C) | It is developed in laboratory | Low V ₁ and sintering T _s , initial matrix is crystalline | Poor technology development |
| 9 | Chromite-niobate + basalt + B ₂ O ₃ (mineral-like) | 1000-1100 | 30-40 | $10^{-7} - 10^{-9}$ $n*10^{-7}$ | Cold pressing and sintering, hot pressing (it is possible to decrease T up to 700-800°C) | It is developed in laboratory | Low V ₁ and sintering T _s , initial matrix is crystalline | Poor technology development |
| 10 | Ferro-silicate (glassy) | 1500 | ~65 (SRW) | $6*10^{-7}$ | IFCC | It is developed in laboratory | High SRW content, low V ₁ | Poor technology development, high sintering T _s |
| 11 | Sodium-silicate (glassy) | 1230 | ~30 (SRW) | 10^{-6} | IFCC, EF-500/1p | It is developed in laboratory | | Poor technology development |