DIFFERENT TYPES OF GROUND-COOLED FERROUS SLAG AS BINDING MATERIALS OF NATURAL SOILS FOR ROAD BASE CONSTRUCTION [1]

Vsévolod Mymrin[2]
Haroldo Ponte[2]

Abstract
Different types of ground-cooled ferrous slag (blast furnace, open hearth, electric steel and converter) have manifested unequivocal binding properties during hydration. Physicochemical processes of hydrated slag interaction with different (mainly clayey) types of soils were studied by wide range of traditional and novel methods during up to 6 years of the samples age. Mainly amorphous new formations grow during the hydration and strengthening of ferrous slag with natural soils and with or without activators (additions of 2-3% of Portland cement or lime). Strengthener slag-soil materials have shown good performance indices (one year strength till 14.4 MPa, high water and frost resistance, etc.). Therefore activated slag-soil materials can be used for the construction of road bases, airfields, levee and dam cores, municipal and industrial dumps, building foundations, etc. Almost 300 km of roads have been built with such bases in different regions of Russia, including regions with rigorous climates in northern regions of Russia and Siberia.
Key words: Ground-cooled ferrous slag; Natural soils; Chemical interaction.

DIFERENTES TIPOS DE ESCORIAS FERROSAS AR-RESFRIADAS COMO MATERIAIS LIGANTES PARA CONSTRUÇÃO DE BASES DE ESTRADAS

Resumo
Diferentes tipos das escórias ferrosas resfriadas no solo (Alto forno, processos Siemens-Martin, Forno de arco elétrico e conversores) têm apresentado incontestáveis propriedades de ligantes durante hidratação. Processos físico-químicos de interação de escórias hidratadas com diferentes tipos de solos (principalmente argilas), ao longo dos seis primeiros anos de produção de amostras, são estudados por grande número de métodos tradicionais e inovadores. Atenção especial tem sido dada à formação de novas fases amorfas durante processo de hidratação e aumento de resistência das escórias ferrosas com solos naturais, com e sem ativadores (adição de 2-3% de cimento Portland ou cal). Materiais Solo-Escória fortalecidos têm apresentado bons índices de desempenho (endurecimento por um ano até 14.4 MPa, alta resistência a absorção de água e a congelamento, etc). Desta forma, materiais Solo-Escória ativados podem ser utilizados para a construção de bases de rodovias, pistas de aeroportos, barragens, aterros municipais e industriais, fundações de construções, etc. Cerca de 300 km de estradas já foram construídos utilizando este material como base em diferentes regiões da Rússia, incluindo regiões com condições climáticas extremamente rigorosas do Norte da Rússia e Sibéria.
Palavras-chave: Escórias ferrosas resfriadas no solo; Solos naturais; Interação química.

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2 *Laboratório de Tecnologia Ambiental, Universidade Federal do Paraná (UFPR), Curitiba, Brasil.*

1 INTRODUCTION

The strengthening of natural soils is ancient problem of mankind. Usually for these goals different organic and inorganic binding materials are used. Most spread inorganic materials are petroleum, bitumen, pitch, etc. Inorganic binding materials which are used for this goals are Portland Cement or Cement kiln dust or lime,[1,2] water glass or calcium chloride,[3] ash[4,5] etc.

Utilization of ground-cooled ferrous slag (GCFS) of different metallurgical processes is one of the biggest environment protection problems for majority of countries with developed metallurgical industry. Even in Europe with the best environment protection legislation every year 35% of produced steel slags are still dumped.[6] Some dumps near metallurgical plants contain till 180 000 000 tons of ferrous slags (Magnitogorsk, Russia).

Exists huge international literature on very different ways of metallurgical slag utilization as cementing materials.[7] The greatest consumer of the slag as inert material instead of crushed natural stone, gravel and sand mixtures are road constructors.[8] Another wide spread way of slag utilization is for Portland Cement production.[9] It is well known technologies of slag-wool production for the thermal and acoustic isolation, for technical glasses, as fertilizer for agriculture purposes, for stabilization of shores,[6] etc. Some authors propose to use it for the coating of environmentally dangerous materials,[1] etc.

Unfortunately, most of the publications concentrate on the use of granulated ferrous slags, which are not strictly industrial wastes, but intermediate product of Portland Cement production.

The method elaborated[11-14] and described in the paper allow to utilize GCFS as binding materials for different natural soil strengthening.

2 MAIN PORPOSES OF THE RESEARCH

1. to study hydraulic activity of GCFS of different metallurgical processes (blast furnace, open heart, converter and electric steel);
2. to research the possibility of significant increasing of it manifestation velocity by small (2-3%) adding of Cement;
3. to develop new environment friendly and financially high effective construction materials from the mixtures of different natural soils with activated GCFS of different metallurgical processes.

3 SUBJECTS OF THE RESEARCH

It were used the most typical GCFS of ferrous metallurgy (blast furnace, open-hearth, converter and electric steel smelting). As the objects of reinforcement were used different natural soils (light and heavy loams, fine and medium sands, loess and loess-like loam). Main components of their chemical composition are presented in the Table I.

Table I. Main components of the chemical composition (%) of GCFS and natural soils under study.

Item	Slags & Soils	SiO_2	MgO	CaO	Al_2O_3	MnO	FeO + Fe_2O_3	SO_3 common	M_a
1	blast furnace	35.2	3.5	36.1	10.6	2.0	4.0	3.7	0.69
2	open hearth	17.5	18.1	26.7	6.1	2.0	22.1	0.2	1.85
3	converter	19.5	1.8	56.1	2.1	6.7	11.0	0.1	2.67
4	electric steel	18.4	16.5	29.6	10.9	4.2	16.2	0.5	1.57
5	light loam	73.2	2.3	3.7	8.8	0	3.2	0.0	-
6	heavy loam	59.1	2.2	8.0	13.4	0	4.6	0.2	-
7	loess-like loam	56.7	2.1	17.4	14.3	0.1	4.4	0.5	-
8	loess	59.1	1.9	6.8	14.5	0	5.8	0	-
9	medium sand	92.7	0.1	0.2	2.3	0	4.1	0	-

Where: modulus of alkalinity $M_a = \dfrac{CaO + MgO}{SiO_2 + Al_2O_3}$

So great difference in chemical compositions of slags under study (Table 1) explains by significant difference in metallurgical processes and the demands to produced final metal. The biggest difference can be seen between the compositions of blast furnace and converter slags, especially in the quantity of SiO_2, CaO, Al_2O_3, MnO, FeO +Fe_2O_3, S common. Compositions of open heart and electric steel slag are more similar to each other (except the quantity of Al_2O_3 and FeO +Fe_2O_3) and located between this two first slags.

This difference in chemical compositions of all slags leads to different values of modulus alkalinity M_a, which is one of the most important indicator of binding properties of inorganic materials. The better M_a belongs to converter slag and the worst – to blast furnace slag.

Maximal SiO_2 quantity occurs naturally in all types of natural soils, but especially in medium sand (item 9).

For the activating of the slags' binding properties and increasing of the velocity of chemical interaction of slag-soil mixtures it were used small (2-3%) of Cement.

4 METHODS OF THE RESEARCH

A wide range of traditional and novel methods of research was used, which complimented each other, in the studying of initial components' compositions and temporal changes of compositions of the newly formed substances during materials strengthening, namely: defining the limit of strength in uni-axial compression and rupture by the Brazilian method, temporal changes of moisture and linear deformation, water and frost resistance, XRD analysis by powder method, the quantity of bound water and carbonates content by TGA and DTA, scanning electron microscopy and chemical analysis (free CaO, SiO_2 , $Fe_2 O_3$, $Al_2 O_3$, non-bounded SO_3 , pH and others), infra-red spectroscopy, X-ray-spectral analysis on "Cameca", "Edax" and "Link-System", Laser micro-mass analysis on "LAMMA-1000". It was impossible to present all of this methods results (namely XRD, DTA, IRS, some chemical analysis, etc.) here because of the article's strict limits, but they are taken into consideration during the description of the process of the materials strengthening.

The samples of the materials were formed under conditions of optimal humidity (10-12%) at a pressure of 10 MPa during 1 min. Hardening occurred in conditions of 98% humidity.

5 EXPERIMENTAL RESULTS

5.1 Dumped Ferrous Slags Hardening Without Activation

More quick and constant increasing of the strengthening of hydrated slag samples demonstrates converter slag (Fig. 1, curve 4). To the age of one year its strength reach 40 MPa. Such result can be expected due to its chemical composition: big quantity of CaO – 56.1% and 1.8% of Mg and relatively small quantities of SiO_2 - 19.5% and Al_2O_3 - 2.1%, and as result – the value of M_a=2.67.

Electric steel slag shows the best strength to the 28th day (3.9 MPa), but the worst (16.2 MPa) on the 6th year .

Very competitive between each other in every stage of hardening was strength of blast furnace and open heart steel, but to the end of the 6th year they were practically equal – near 20 MPa.

5.2 Strength Results of Dumped Ferrous Slags after Activation

Small quantity of Cement or lime (2%) was used to increase common alkalinity of the hydrated slags. Because it is rather difficult to think about so small quantity of them as independent binding materials.

Figure 2 shows the alterations in the hardness of GCFS of different processes, activated by 2 % of Portland Cement. The comparison of the same slags strengthening without activator (Figure 1) significant increasing of hardening velocity as result of activation, especially in the first year.

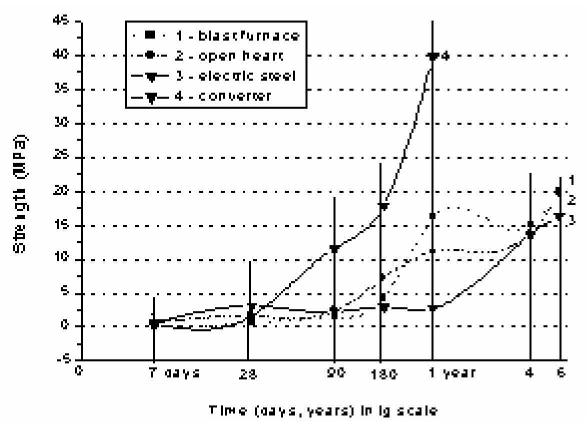

Figure 1. Strengthening of hydrated GCFS of different metallurgical processes without activator: 1 – Blast Furnace, 2 – Open Heart, 3 – Electric Steel, 4 – Converter.

The only exception of this rule is open hearth slag (Figures 1 and 2, curves 2), which decreased his strength almost twice (from 7.2 till 3.8 MPa) on the 180th day in the result of activation and almost three fold (from 11.1 till 4.6 MPa) to one year. On the 4th year the difference became less (13.8 versus 11.9), but on the 5th year it increase once more (19.3 versus 9.3 MPa) to decrease a little bit till (19.4 versus 14.4 MPa) on the 6th year.

Even worst result was obtained during the activation of open hearth slag by lime. And only very big quantities of Cement (till 5 %) changed the situation. But in such a case it is impossible to speak about Cement like activating agent, it works as independent binding material.

Blast furnace slag has better result of activation. On the 28th day the strength of activated slag became 3.4 MPa (versus 0.5 of non-activated, i.e. 680%) and on the 90-th day – 5.8 versus 1.4 MPa (i.e. 415%). But the prevalence of activated slag strength decrease from the 180-th day till 5 years till 12-20%

The strengthening effects of converter and electric steel slags activation are more impressive: – the predominance are 2 - 5 times till one year age of the samples.

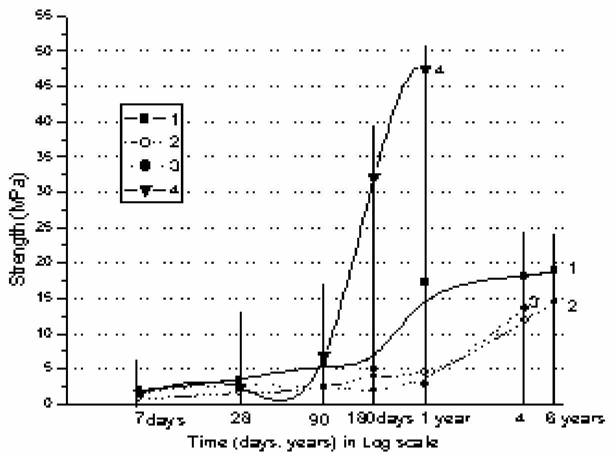

Figure 2. Strengthening of hydrated GCFS of different metallurgical processes activated by 2% of Portland Cement: 1 – Blast Furnace, 2 – Open Heart, 3 – Electric Steel, 4 – Converter.

5.3 Natural Soils Strengthening by Activated Gcfs

Mechanical properties of slag-soil materials depend mainly of the properties of all its components chemical compositions of (Table 1), its ratios and interaction in alkaline pore solutions. Almost all of the soil-slags materials without activator have very little values of strength on the 90th day and water resistance. All of them (uneven items of Table 2) failed frost resistance tests. Only samples of mixture 7, Table 2 (medium sand + open hearth slag) had not effect of spontaneous decomposition till the end of frost resistance tests. But the value of C_f (0.42) allow to use this material only as substratum of road base.

But small (2-3%) addition of Cement made their mechanical properties unrecognizable. The strength (Figure 3) of the materials to the 90-days-age differs from 1.87 MPa (curve 3 - light loam + open hearth slag +3% P.C.) till 11.98 MPa (curve 6 - loess + electric steel slag +2% P.C.). Water and frost resistance of all slag-soil materials (Table 2) also improved to a high degree as a result of the activation by P.C. and to 360-days it changed from 3.63 (curve 1 - light loam + blast furnace slag +2% P.C.) till 14.43 MPa (loess + electric steel slag +2% P.C.).

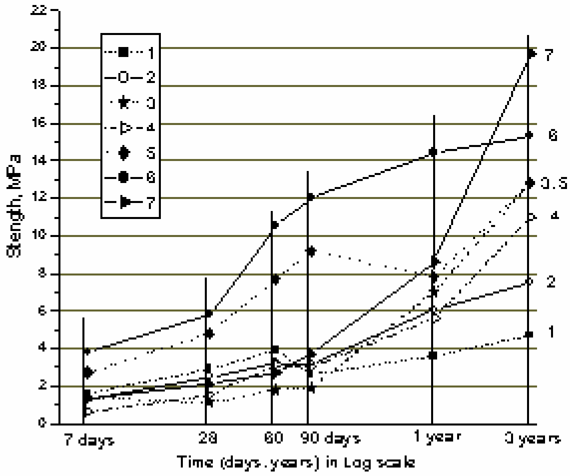

Figure 3. Resistance changes of natural soils strengthened by activated GCFS, where 1 - light loam + blast furnace slag, 2 - heavy loam + blast furnace, 3 - light loam + open hearth, 4 – medium sand + open hearth, 5 – loess-like loam + electric steel, 6 – loess + electric steel, 7 - heavy loam + converter slag

Table 2. Water and frost resistance effect of natural soils strengthening by GCFS, activated with Portland Cement (P.C.).

	Materials composition	R_a	C_w	R_f	C_f
1	Light loam + blast furnace slag	0.57	0.44	0	0
2	the same +2% P.C.	2.48	0.96	2.08	0.84
3	Heavy loam + blast furnace slag	0.09	0.37	0	0
4	the same +2% P.C.	2.91	0.96	2.30	0.79
5	Light loam + open hearth slag	0.06	0.24	0	0
6	the same +3% P.C.	1.74	0.93	1.50	0,86
7	Medium sand + open hearth slag	1.30	1.71	0.72	0.42
8	the same +3% P.C.	3.37	1.04	4.08	1.16
9	Loess like loam +electric steel slag	3.66	0.97	0	0
10	the same +2% P.C.	9.57	1.16	7.96	0.83
11	Loess + electric steel slag	3.37	0.84	0	0
12	the same +2% P.C.	13.9	1.14	11.1	0.81
13	Heavy loam +converter slag	3.12	0.93	0	0
14	the same +2% P.C.	4.26	1.14	3.32	0.78

Where: C_w and C_f - coefficients of water and frost resistance of samples; R_w - strength of 90-days samples saved in air-humid conditions (94-96% of humidity) after water saturation during 24hours; R_f - strength of water saturated sample after 25 cycles of freezing and thawing (-25°C and + 20°C in water), each cycle - 16 hours.

After the activation all of them can be recommended as road base materials in accordance to above mentioned Russian construction standards.

5.4 Structure Formation of Slag-soil Activated Materials

The processes of the hardening of the mixtures natural soil – GCFS – activator were studied with all instrumentally possible details in accordance to the paragraph 4 “Methods of research”. Main part of obtained physicochemical parameters of strengthening of the system “heavy loam - blast furnace slag – 2% of Portland Cement” is presented in the Table 3.

Similar data were obtained also for all the compositions, presented in the Table 2, but they were not given here only because of the economy of the article place.

It can be seen from the data of Table 3 that:

1. the most quick increasing of the system’s values happens during first 7 days,

2. exist clearly defined synchronization between the changes of compression resistance and losses of bounded water of samples during all 3 years under study,
3. this changes coincide till the 60th day with the value of pH and overlap till 3 years,
4. the values of the coefficient of lineal deformation and contains of CO_2 and SiO_2 increased steadily during all time under study, but in the first 60 days (i.e. 5.5% of this 3 years) they rise on 61.7%, 54.6 and 39% correspondingly of their final values.

Table 3. Changing of the indices of heavy loam strengthen by activated blast furnace slag

Indices	Time of hardening								
	Ini-tial	Days					Years		
		7	28	60	90	180	1	2	3
Compression resistance, MPa	-	1.3	2.5	3.2	3.1	4.4	6.0	5.7	7.5
Coefficient of lineal deformation, %	-	0.74	1.04	1.13	1.22	1.37	1.35	1.70	1.83
Common losses of weight, (TG), %	-	10.33	10.73	11.50	11.33	11.45	11.67	11.74	13.83
Contain of CO_2, (TG),%	-	1.00	1.00	1.00	1.33	1.33	1.34	1.52	1.83
Losses of bounded water, (TG), %	-	9.33	9.73	10.50	10.00	10.12	10.33	10.22	12.00
pH	10.9	8.41	8.25	8.21	8.34	8.45	8.31	8.02	7.70
Content of mobile SiO_2, %	0.23	0.60	0.62	0.62	0.65	0.70	0.70	1.15	1.40

Except, in XRD no new peaks of new formed crystals appeared during all the period. But on SEM (Figure 4) it is possible to see a lot of new gel-like formations, completely covering all sample surface.

All this data can be explained by the corrosion of soil and slags solid surfaces by alkaline (pH=10.90) pore solution, by carrying out of all ions of solved parts into this solutions, with transformation of sol solutions to more dense gel.

Part of Ca and Mg ions are binded in very different complex compounds of new formations and partly they are binded by CO_2 of air in the carbonates. But carbonization process is going very slowly. It reaches the value 2.3% of $CaCO_3$ on the conversion of CO_2 content on the 60th day, 3.0% - to one year and 4.2% to 3 years. So small summary quantity of all carbonates forms (calcite, dolomite, siderite, etc.) is hardly enough for their peaks fixation by powder XRD method and its sensibility (near 3-5%).

The fact of samples strengthening till almost 20 MPa in the case of the absence of other new crystal peaks on the XRD curve can be explained only by two possibilities:

1. growing up of some crystal phases, but in small quantity each, less than sensibility of XRD method. But results of SEM (Figure 4) refuse this possibility, because all surfaces of the materials are covered only by amorphous-like new formations without some similarity to crystal bodies;
2. by growing up of amorphous new formations with its gradual transformation to a stone-like condition.

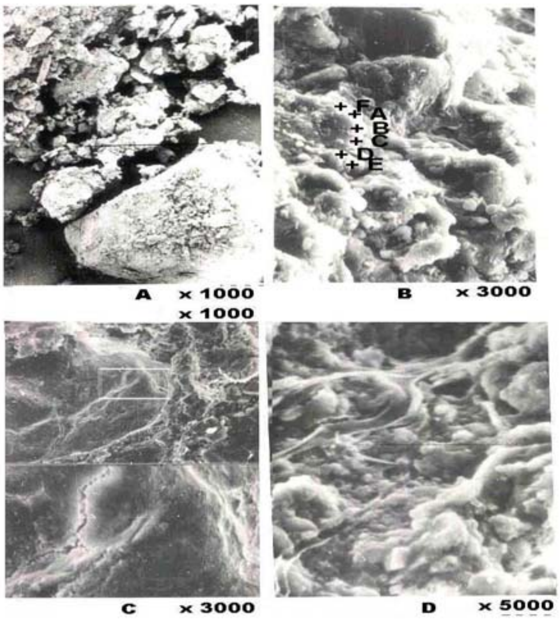

Figure 4. SEM image of the Blast Furnace Slag: A – before hydration, B – after 28 days of hydration, C – after 180 days, and D – after 6 years of hydration.

Note: on photo 4-B – LAMMA-spectra points A-F on the surface of new formations (Figure 5).

In the beginning of the hydration process the density of the pore solution is rather low, but it increase with a time. And it looks like the density of new formation around solid surfaces of the slag after first year became dense enough to prevent future strong erosion of slag's particles by alkaline pore solutions. Due to this cracks of syneresis liquid phase of alkaline pore solutions approaches the surface of solid slag particles and began to leach them out. During the period 90 – 180 days the cracks are closed by more fresh generation of new amorphous gel formation.
This effect of the cracks closing can be seen due to the filling of their trenches by amorphous materials and the appearance of forms like parapets on the both sides of them.

Amorphous nature of new formation can be proved by:

1. the absence of new peaks on the XRD till the samples age 6 years, except very small peaks of the carbonates;
2. above mentioned absence of crystal-like forms of SEM (Figure 4) and the presence of specific cracks of syneresis and its closing with a time by new portions of gel;
3. the presence of wide exothermic areas between 180^0 and 750^0 C on DTA curves of all ages;

4. the results of laser micro-mass analysis (Figure 5 – A-F). All of obtained spectrums of chemical compositions of all nearest points of new formations are quite different (typical on the Figure 4- A, B, C) in the combination of the isotopes and their quantity. The same results were obtained with X-ray analysis on “Cameca”, “Edax” and “Link-System”, which are not presented here.
Nevertheless, after 90 days the strength, water and frost resistance of the materials met the requirements of standards for the second (2-4 MPa) and the third (1-2 MPa) grades of reinforced soils.

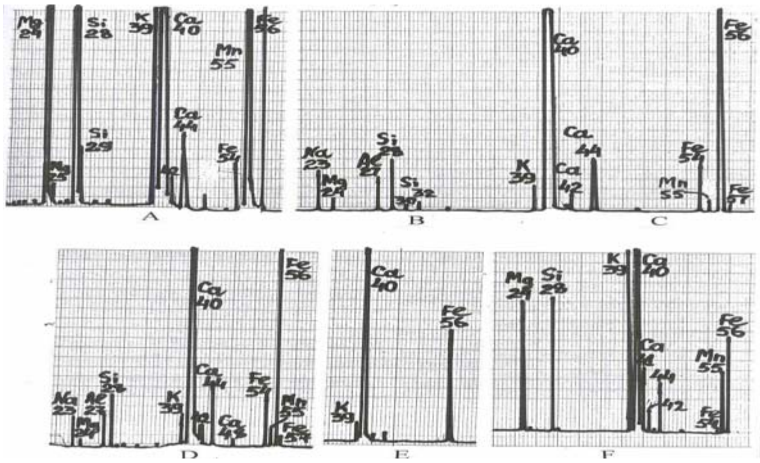

Figure 5. Typical Laser Micro-Mass Analytic (LAMMA) specters of new formation (Figure 4-C) on the 180th day of heavy loam - blast furnace slag – 2% of Portland Cement hydration.

Future increasing of the material resistance from 4.4 till 6.0 MPa in the period 180 days – one year, in our opinion can be explained by the synthesis of the gel of new formation in the bottoms of the cracks of syneresis. The increasing of new gel arise the quantity of bound water from 10.12 till 10.33%. Alkaline corrosion of slag's fresh surfaces on the bottom of the cracks leads to the increasing of all ions quantity, including alkaline Ca and Mg. I.e. it leads to the growing up pH value. But the changes of pH value is not so clear synchronous with the resistance and bounded water contain.

Well known gel-formation property as SiO_2 was the main reason of strong effect of mechanical properties increasing after the mixing of open hearth slag with medium sand. This mixtures became most frost resistance as without activator, so with him (Table 2, item 7 and 8).

The same simultaneous oscillation observe in the periods 1-2 and 2-3 years with total growing up of this two parameters. It happens because of the total increasing of the gel formation without significant lineal deformation of the samples, i.e. due to common growing up of this gel density. Such gluing of solid slag and soil grains by gel formation with the growing up of density explains the effect of common increasing of the samples resistance and other mechanical properties, like water and frost resistance.

6 MATERIALS APPLICATION

Leaching tests of the materials in acid, alkaline and natural solutions were conducted by two independent competent medical and sanitary expert groups. The value of leachability is well below of the demands of international standards. Results of the leaching tests and high value of main mechanical properties of slag-soil activator materials allowed to recommend them as road base construction materials instead of crushed stone, gravel, sand, etc.

First constructions of experimental pieces of roads of different technical categories showed its highly economical efficiency and exploitation properties even in extremely rigorous climate conditions of Russian North and Siberia. After that some hundred kilometers were constructed with different road structure. The comparison of traditional; and proposed structure are given on the Figure 6. Two layers (crushed stone and sand) are replaced by layer of the new activated slag-soil mix.

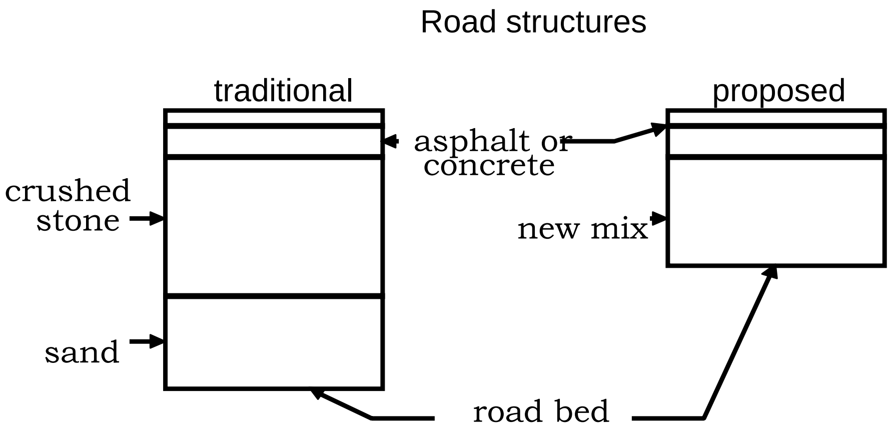

Figure 6. The comparison of the simplest schemes of traditional and proposed road structures.

The construction of the road bases layers are made by mixing natural soils with GCFS, activator and water directly on the road (“in situ”). The mixture can be prepared in stationary mixers too.

7 CONCLUSIONS

1. GCFS of all metallurgical processes under study (blast furnace, open-hearth, converter and electric steel) has clearly defined binding properties. But their development is so slowly, that only open hearth slag can be used as independent material without Cement activating additions.
2. The acceleration of slag’s binding properties is easily available by the adding of 2% Portland Cement.
3. The process of strengthening of all types of ferrous slags under studying have place due to synthesis of amorphous new formation. Only very little quantity of carbonates are formed as crystal structures, but they can not be responsible for the samples strengthening till 47 MPa to one year age.
4. The strengthening of the system “slag-natural soil-activator” has the some amorphous nature. But natural soils are adsorbed significant part of alkaline ions Ca and Mg, that is why alkaline excitement of solid parts is going with considerably low intensity, synthesis of amorphous new formations is more weak. As the result, the best value of one year strength of this system is only 14.4 MPa.
5. Activated slag-soil materials can be used for the construction of the bases of roads, airfields, municipal and industrial dumps, as dam core, etc. Some hundreds of roads were constructed with such bases in different regions of Russia, including rigorous climate zones of Russian North and Siberia. All of them show a lot of advantages in comparison with world traditional way of roads construction, its high technological, economical and ecological efficiency during almost 30 years of exploitation.

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