Physicochemical Processes of Metal Lixiviation in the Disintegrator

V I Golik[1], A B Efremenkov[2]

Doctor of Technical Sciences, Professor,
[1]North-Caucasian State University of Technology, Russia, 362021, Vladikavkaz, 44 Nikolaev str.,
[2]Yurga Institute of Technology, TPU affiliate, 26, Leningradskaya Str., 652055, Yurga, Russia

E-mail: vigolik@mail.ru, abe73@rambler.ru

Abstract. The results of lixiviation-based recycling of ore mill tailings in the high-speed disintegrator are presented. The regularities of the change in properties are defined, as well as control directions over them via alteration of variable processing factors are defined. The model to determine the economic effect of the use of solidifying mixes based on mill tailings is proposed. The model of perfectly mixing reactor cascade in continuous operating conditions is developed to describe activation on minerals in the disintegrator.

Introduction

Over the last two centuries, the issue of removing mill tailings of excavated mineral resources from the ground has become urgent on a global level, and made other vital tasks of the mankind less important [1].

Although we are conscious of the necessity to protect our environment from metal and salt pollution – products of natural lixiviation of minerals, physicochemical fundamentals of recycling technologies are developed insufficiently. New technologies to produce and process mill tailings can hardly solve the key problem of wastelessness.

Improperly developed methods for study on materials in order to control them are considered to be the reasons for practice lagging behind the science in this important field.

Technologies of ore dressing are not so developed as those of ore excavating, as the consequence, hundreds of millions tons of tailings are accumulated on the Earth surface.

As the competition in mining industry gets stronger, toughening the requirements for excavated mineral resources, creating artificial masses made of solidifying mixes gets an integral part of underground field mining of commercial minerals. Cement is used as a binder in the basic variant of their preparation, and excavated natural materials – sand and gravel mix as a nonreactive aggregate.

At the industrial enterprises there are accumulated production residues (ashes and slag of thermal power plants, mill tailings of ores, overburdens and off-grade ores etc.), their chemical-mineralogical composition is similar to that of natural resources used for stowing. These man-made materials somehow yield to standard materials in activity or initial reaction rate because of natural or anthropogenic impact [2].

As numerous studies have highlighted, the increase in activity of man-made materials is made possible not only by specific surface when processing in mills, but by growing unsoundness of the lattice, occurring both on the surface of material and in bulk of its elementary particles due to "active lattice" formation while being processed in the disintegrator [3].

Processing in the disintegrator at the impact velocity of particles 160 m/s (12000 revolutions a minute) goes with the growth of specific surface of materials by 35-150 %. The increase in specific surface is conjoined with solubility of substances contained in the additives to the cementing material. Fine grinding of materials in the disintegrator furthers formation of solid homogenous structure of cement stone while their aqueous suspensions are hardening.

Materials, which were considered inert before, e.g. mill tailings of metal ores, become hydraulically active. The texture of hydrated new growths with incorporated hydrosilicates among non-hydrated particles and crystals of new growths is more compact than that of base cement stone. Hydrosilicate fibers overlap pores, which are dimensionally smaller than those of standard cement stone.

The increase in solidity of cement stone produced at the temperature below 30^0C is higher over the first 24 hours in comparison with conventional methods of intensifying processes: the time of hardening goes up to 28 days or the temperature grows up to 75^0C for standard samples. The solidity of samples produced from activated materials is 2-4 folds higher than that of standard samples.

Mechanochemical activation of cement affects the processes of structure formation and the mechanism of gain in strength of cement stone. Simultaneous activation of cement and ash causes the rise of concrete strength by 20-30%, whereas ash or cement activated separately increase the strength in the interval 5 to 10%.

Processing in the disintegrator involves dimensional rearranging of particles. The products of the disintegrator contain small fractions of particles over 125-400 μm and under 5 μm. The concentration of chemically bound water is lower in the samples containing man-made cementing materials, than in those of pure cement, due to partial binding of calcium hydroxide by silica of a finely-grinded additive. There is more chemically bound water in binding material based on slag grinded in a ball mill because of fine fraction loss when processing in the disintegrator.

The scientists share the same view, if complex binding materials cement + additive are used, provided that specific surface is equal, processing of an additive e.g. slag is more efficient in the disintegrator than in a ball mill (Tabl. 1) [4].

Table 1. Activity and chemical composition of hydration product

Type of slag processing	Specific surface, cm^2/g	Ultimate compression strength, MPa		Chemical composition of hydration products in a second after steaming, %		
		1 c.	180 c.	H$_2$O$_{x.cB.}$	Ca (OH)$_2$	CaCO$_3$
Standard variant – cement 100%	3500	14	26	9.6	5.6	5.5
Ball mill	4980	14	29	9,0	1.6	3.1
Ball mill	2100	8	17	4.9	1.7	1.8
Single-phase disintegrator	1500	12	22	7.3	2.5	3.2
Double-phase disintegrator	2100	12	20	7.4	2.5	2.5

Note: ratio cement to slag, %: 60:40.

At present, materials grinded to the specific surface 600-4000 cm^2/g and grains below 10 μm are used in mining industry. Backfills, gel powders, weighting materials, chemical reagents, as well as chemically low-active and difficult-to recycle-products of metallurgical, mining, chemical and energy industries are milled this way. Using aforementioned products as components of binding materials in

solidifying mixes requires for their fine dispersion and multi-component mixing, sometimes even making them more chemically active. It is implemented in disintegrators [5].

Intensifying resource saving trends in development of mining industry insist on metal extraction from mill tailings to be recycled as the total cost of lost metals can exceed the cost of extracted ones.

Conventional dressing procedures can't provide extraction of residual metals both from ores and preprocessed mill tailings as 1-2 types of energy impact are used and oriented on extraction of limited amount of mineral components [6].

Materials based on mill tailings of ores are used in mining without extraction of metals from them to fill the used breasts of stopes, e.g. the Korobkovskoye deposit of Kursk Magnetic Anomaly. Here the loss of gold only amounts to 3 tons a year, whereas its concentration in tailings is 0.5 g/t [7]. This practice is considered to be a palliative both in view of economy and environment protection.

An advance of wasteless recycling is in technologies involving metal lixiviation, although chemical lixiviation even though mechanically activated takes a lot of time and does not provide a needed level of extracted metals.

The proposed technology differs from the available mechanochemical one, because basic reagents are not produced from minerals used in the process but fed into the processing chamber of the disintegrator from the outside [8].

In comparison with the standard procedures evolving in recent years mechanochemical technology of recycling mill tailings is distinguished by accelerated metal extraction in the processing chamber of the disintegrator due to the energy resulting from the increase in the speed of rotor revolution and particle impact. Practical value of the phenomenon is in the fact that leaching solutions are not filtrated in the cracks but pressed in them, i.e. metals are extracted alongside with crystal fracturing [9].

In certain conditions reagents – oxidizers extract into the solution merely all metals contained in ores twice as fast as under agitation-based lixiviation. The technology enables to extract metals from mill tailings the way they meet the sanitary requirements, then, secondary mill tailings can be used without restrictions, e.g. for preparing solidifying mixes.

The principle of disintegration is known approximately over 150 years, the phenomenon of lixiviation has been developed since the middle of the last century in uran industry, and the idea of leaching in the disintegrator has been becoming well-known in recent years only [10].

The issue becomes even more topical as environmentally friendly technologies focused on stowing man-made cavities with solidifying mixes have been rapidly developed in mining industry, so mill tailings can be used as raw materials for this purpose.

This paper is aimed at development of complete waste utilization of ore mining and smelting industry via making more precise parameters of physicochemical processes of mechanochemical treatment based on lixiviation in the disintegrator.

Methods of experiment
As the basic method to solve the task experiments were carried out in a laboratory disintegrator, changing state of the substance so it gains a new quality. The parameters of solidifying mixes are studied analytically via comparing traditional technologies of preparing mixes with an alternative procedure based on lixiviation in the disintegrator.

Experimental study on metal extraction based on lixiviation and recycling of mill tailings involve comparing strength factors of conventionally prepared mixes and those ones based on lixiviation in the disintegrator in various conditions of processing, inter alios:

- agitation-based lixiviation in the percolator;
- agitation-based lixiviation in the percolator of preliminary activated dry mill tailings in the disintegrator;
- lixiviation of mill tailings with reagents in the processing chamber of the disintegrator;
- agitation-based lixiviation of mill tailings, which are activated once with reagents in the disintegrator;

- lixiviation of mill tailings, which are activated repeatedly in the processing chamber of the disintegrator.

Variable factors, adjustable when carrying out experiments:

1. Concentration of reagents: sulfuric acid and sodium chloride.
2. Liquid and solid phase ratio (L:S).
3. Time of activation-based lixiviation.
4. The speed of rotor revolution in the disintegrator.
5. The number of processing cycles.

The assessment criterion of samples under consideration is extraction of metals specified in the course of analyzing the samples taken from the disintegrator every hour and at the end of lixiviation process, as well as uniaxial compression strength of solidifying mixes, produced from ferruginous quartzite mill tailings of Lebedinskoye Deposit.

The solidifying mix with constant chemical composition, kg/m^3 are tested: mill tailings possessing diverse parameters of activation – 1445, water – 380, cement – in dependence on conditions of research.

Results

The strength of conventionally produced solidifying mixes without lixiviation-based extraction of metals and mechanical activation varies monotonically in dependence on the concentration of binding cement (Table 2).

Table 2. The strength of not activated solidifying mixes

Consumption of Portland cement, kg/m^3	30	60	80	100	120	180
Strength, MPa	0.79	0.92	0.101	1.20	1.41	1.80

Mechanical activation of mill tailings in the disintegrator increases the strength of the solidifying mix (Table 3, Point 2).

All modes of lixiviation support metal extraction and reduce the strength of solidifying mix as moisture increases (Table 3, Points 3 – 5), its compensation is possible through raising frequency of processing (Table 3, Point 6).

Table 3. The strength of binding cement mixes relative to activated mill tailings

№	Activation type	Strength, MPa, 24 h.		
		7	14	28
1	Not activated, consumption of Portland cement 100 kg/m^3	1.04	1.11	1.20
2	Reagentless mechanical activation	1.16	1.25	1.32
3	Agitation-based lixiviation without activation	0.52	0.61	0.72
4	Reagentless mechanical activation with agitation-based lixiviation	0.68	0.73	0.88
5	Mechanochemical activation in the disintegrator	0.73	0.77	0.94
6	Three-phase mechanochemical activation in the disintegrator	0.92	1.10	1.22

The strength of the mix under three-phase mechanochemical activation of mill tailings in the disintegrator is similar to that of the basic mix, 100 kg/m^3 ready-made Portland cement is consumed.

Mechanical activation of mill tailings in the disintegrator without reagent lixiviation increases the strength of cementless mixes by 10 and more per cents (Table 4, Point 2). Liquid medium of lixiviation in the disintegrator and agitation vat deteriorates the strength and requires for increase in the frequency of processing to provide the same strength (Table 4, Points 3-6).

Table 4. The effect of activation on strength of cementless mixes

№	Activation type	Strength, MPa, 24 h.		
		7	14	28
1	Not activated	0.64	0.81	1.01
2	Reagentless mechanical activation	0.86	0.95	1.12
3	Agitation-based lixiviation without activation	0.42	0.57	0.62
4	Reagentless mechanical activation with agitation-based lixiviation	0.60	0.69	0.78
5	Mechanochemical activation in the disintegrator	0.63	0.71	0.84
6	Three-phase mechanochemical activation in the disintegrator	0.82	1.00	1.12

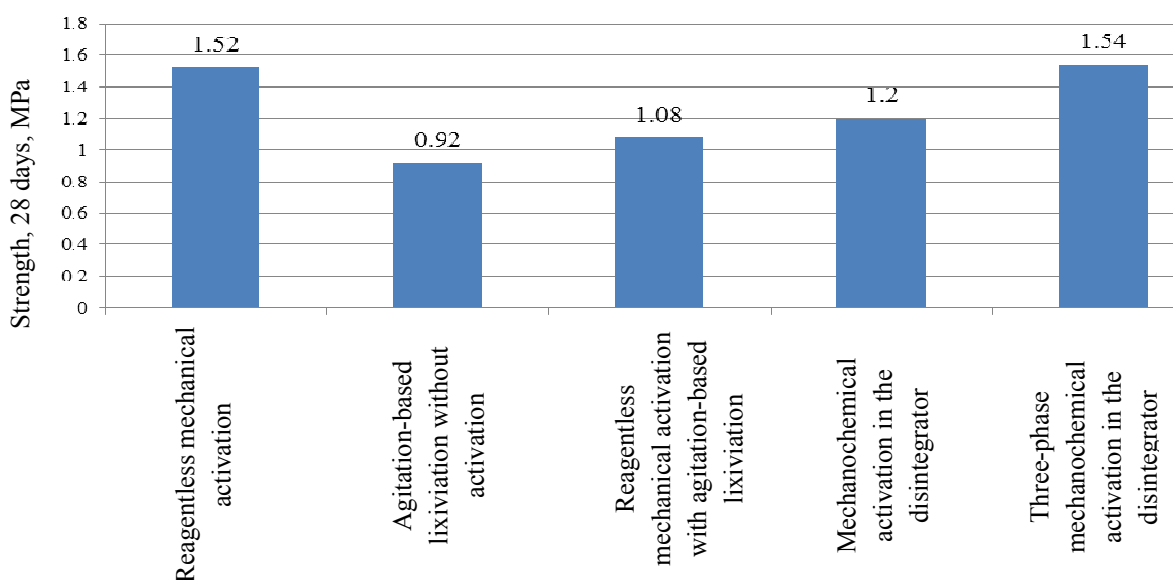Solidifying mixes containing unlixiviated mill tailings activated in the disintegrator and cement (Figure 1).

Figure1. The strength of solidifying mix with cement

Activation increases the strength of the mix (Table 5, Point 2). In all conditions of lixiviation the strength gets reduced when one-phase processing and is compensated by its frequency (Table 5, Points 3-6).

The strength of mill tailings activated without cement in the disintegrator is lower by 20-25% (Figure 2), its compensation by frequency of processing is still possible (Table 5, Points 1-6).

Table 5. Parameters of activation

№	Activation type	The strength, 28 days, MPA		
		cement100 kg/m^3		Cementless activation
		Not activated	Activated	
1	Not activated	1.30	-	1.01
2	Reagentless mechanical activation	-	1.52	1.22
3	Agitation-based lixiviation without activation	-	0.92	0.62
4	Reagentless mechanical activation with agitation-based lixiviation	-	1.08	0.78

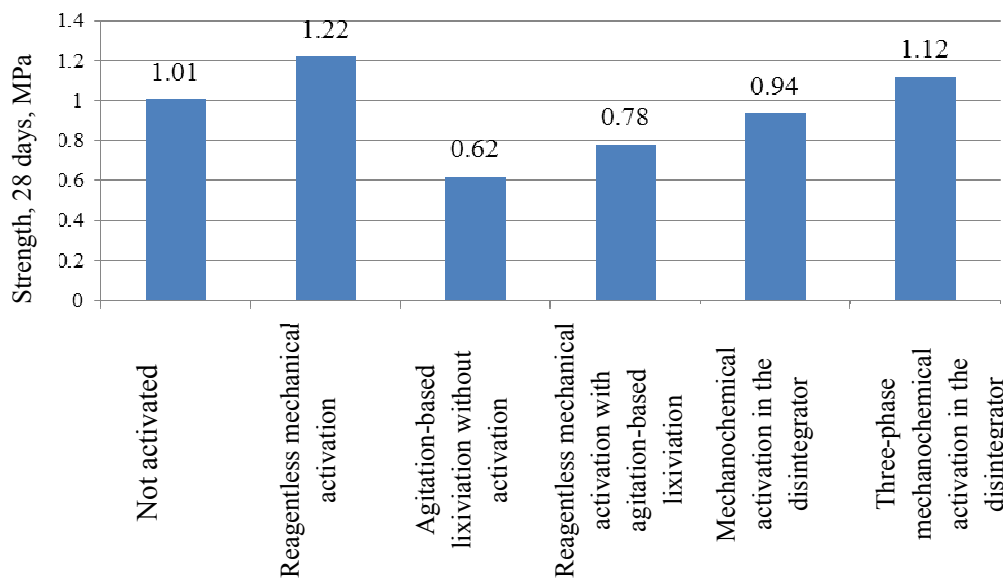| №	Activation type	The strength, 28 days, MPA		
		cement100 kg/m^3		Cementless activation
		Not activated	Activated	
5	Mechanochemical activation in the disintegrator	-	1.20	0.94
6	Three-phase mechanochemical activation in the disintegrator	-	1.54	1.12

Figure 2. The strength of cementless solidifying mix

The cementless compounds containing activated in the disintegrator mill tailings possessing the strength 0.5-1.0 MPa can be used as solidifying mixes for stowing man-made cavities in corresponding geo-mechanical conditions [11].

The gain coefficient of strength of solidifying mixes based on activated in the disintegrator mill tailings is estimated 20-30%.

The importance of the disintegrator in the outlined above technology consists in the increase of the strength of cementless solidifying mixes containing mill tailings. This task is well-performed by the disintegrator as the strength of the thrice-processed mix is comparable with that of the mix containing ready-made cement [12].

Lixiviation as an integral part of the cycle somehow deteriorates the strength of the cementless compound, nevertheless, enables extraction of residual metals from the mill tailings and makes the recycled tailings safe from the standpoint of sanitary standards and accessible for the wide use [13].

The economic effect of field development using solidifying mixes based on mill tailings over the period of deposit exploitation is:

$$E_{\text{хо}} = (P_{e\text{м}} + P_{\text{хтz}} + P_{\text{хм}}) - (X_{e\text{м}} + X_{\text{тз}})$$

where $E_{\text{хо}}$ − economic effect of the use of mill tailings, rub.;

$P_{e\text{м}}$ − profit from field development, rub.;

$P_{\text{хтz}}$ − profit from tailings used as consolidating stowing, rub.;

$P_{\text{хм}}$ − profit from extraction of metals from tailings, rub.;

$X_{e\text{м}}$ – expenditures on metal extraction from mill tailings, rub.;

$X_{\text{т3}}$ — expenditures on production of consolidating stowing from mill tailings, rub.;

Alongside with mechanochemical activation dispersion and homogenization of multi-component materials are possible in the disintegrator. When processing small mill tailings the function of a high-speed mixer is a foreground one.

The materials of a solidifying mix include low base hydrosilicates with silica. The solubility of particular components of the material can be increased via processing in the disintegrator. The concentration of calcium hydroxide in the liquid phase at the temperature over 50^0C during the first hours depends on the mode of its dry disintegration. When solidifying of not activated mix the residual concentration of lime in the liquid phase of cement solution is 760 mg/l at the end of cementation that is nearly equal to its saturated solution in these conditions [4]. After processing in the disintegrator the residual concentration of lime is 470 mg/l at the rotation frequency of rotors in the disintegrator 6000 revolutions a minute; and 180 mg/l – at 12000 revolutions a minute.

Processing of silica-containing materials in the disintegrator supports their activation and with respect to the mode of activation increases the speed of solidifying in the initial phase of hydration. When consolidating activated compounds thermodynamically stable low based hydrosilicate compounds form in the earlier periods of consolidation as compared with the base variant. In terms of thermodynamics free energy of hydration equals to the difference of free energies of input and output products of the process. The lower free energy of formation of input waterfree binding materials is, the higher is the free energy of hydration.

The disintegrator facilitates the destruction of upper layer of material and reduces the energy of waterfree binding material. The difference in free energies of formation of solids subjected to mechanochemical activation can be similar to free generation energy of salts from oxides

As the result of hydrating the substance in the course of mechanochemical activation hydrates with new thermodynamic properties are formed, key factors of them include dissolubility and diffuse characteristics of ions, inter alios, calcium, and silicon acids formed in the process of hydration and hydrolyze.

The ratio of concentration of calcium and silicon acid ions exceeds the unity that is the reason for high basicity of primary hydrated phases. Calcium ions detach from the crystalline structure of the binding material under action of water polar molecules, whereas necessary for formation of hydrosilicate phases bond rapture in silicon and calcium oxides requires for energy of activation.

The bigger particles of silicon acid are, the more important are the diffuse processes and the more energy is consumed for ion interacting. Dispersion of substance particles conjoining with bond raptures decreases the staging of generation of hydrated compounds and facilitates formation of thermodynamic phases.

The process of treatment in the disintegrator is described by the model of perfectly mixing reactor cascade in conditions of continuous operation:

$$\text{A}_{\text{к}} = \text{A}_i + V_d \times \text{A}_i \times t_{\text{к}} \times n$$

where A_i – the initial activity of material;

$\text{A}_{\text{к}}$ – the activity of material in the following phase of processing;

V_d – the speed of changing activity of material;

$t_{\text{к}}$ – the time of material processing in a single cycle;

n – the number of processing cycles.

Conclusions

The efficiency of physical-mechanical processes taking place in the course of mechanochemical technology is specified via comparing strength factors of mixes and extraction of metals in different operating conditions of the disintegrator.

Activation of mill tailings and lixiviation of metals from them in the disintegrator meet general requirements and are to be controlled by changing variable factors of processing.

Low-cement and cementless compounds based on activated in the disintegrator mill tailings possessing the strength 0.5-1.0 MPa can be used as solidifying mixes for stowing man-made cavities

in corresponding geo-mechanical conditions. The gain coefficient of strength of solidifying mixes containing mill tailings activated in the disintegrator is estimated 20-30%.

The process of treatment in the disintegrator is described by the model of perfectly mixing reactor cascade in conditions of continuous operation. The economic efficiency of the new technology is specified by the volume of replaced ready-made components by secondary recycled mill tailings subjected to mechanochemical processing and selling simultaneously extracted metals.

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