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## THERMOMECHANICAL ASPECT OF SELECTIVE FLOTATION OF SPHALERITE AND PYRITE



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Selective flotation is one of the most complex activities in mineral dressing as sulfides and copper, zinc and iron have very similar flotation properties and intergrow very finely; in addition, one and the same area of an ore body can be composed of ore of different industrial grades. Considering material constitution of copper–zinc ores, dressing involves complex multibranch flotation circuits with separation of copper and zinc “head” concentrates, a few bulk flotation stages, selective cycle with the bulk concentrate, zinc cycle of flotation, and, frequently, cycle of final concentration for zinc concentrate [1].

Improvement of the reagent regimes in the cycles with separation of copper “heads,” copper–zinc flotation and the cycle of selection for copper–zinc concentrates is achieved by finding selective collectors relative to pyrite and zinc in separation of copper and zinc minerals from pyrite [2]. However, with selective reagents in copper flotation, amount of sphalerite and fine-ground pyrite grows in the zinc flotation cycle, which mutilates flotation process. It is known that zinc cycle of copper–zinc ore flotation uses xanthate modifications that are not selective relative to pyrite. In view of the aforesaid, it is required to design a process flow chart toward higher efficiency of separation of zinc minerals and pyrite in the zinc cycle of flotation.

It has been shown in [3] that it is efficient to prepare sphalerite and pyrite for selective flotation with a thermomechanical treatment package, including attrition. Under conditions being analogues to flotation, effect of attrition on the surface of sphalerite and pyrite has been studied with infrared spectroscopy used in analysis of complex multicomponent systems and allowing determining composition and bonding in the subsurface layer and estimating crystallinity of specimens after physico-mechanical treatment. Infrared spectra of diffuse reflection of powdered sphalerite and pyrite were re-

*The article reports the research into purposeful alteration of surface properties of sphalerite and pyrite using a package of thermomechanical actions. The technology of zinc concentrate quality improvement without zinc recovery reduction has been developed and recommended for modernization of operating copper-zinc ore processing plants.*

*The experimental data on copper-zinc ore flotation have shown that sphalerite and pyrite present at the final process stages of collective-selective flotation possess equal kinetics of floatability. This is particularly obvious in zinc flotation cycle, where pyrite is only depressed with lime and blue copperas activates both sphalerite and pyrite, which results in that quality of zinc concentrate is not higher than 46–48%.*

*It is known that flotation behavior of sulfide minerals depends on the strength of the bond between a collector and a mineral surface adsorption property of which is governed by energy condition of the surface atoms. In fine grinding down to first tens of micron, the surface of sulfide minerals undergoes significant changes both due to deformation and decrystallization of crystalline structure, and as a consequence of oxidation of newly formed particles and sorption of cation-anion components from fluid phase of flotation pulp.*

*Inclusion of only regrinding in zinc cycle produces no desired output, therefore, one of potential ways of controlling separation of minerals with similar process properties and for improved selectivity of mineral dressing, complementary to modifying reagents, is application of purely physicochemical methods where such techniques as aerification, oxidation-heat conditioning and mechanical activation belong.*

*The authors have studied the flow and mechanisms of a package of physicochemical processes ensuring efficient separation of pyrite and sphalerite and higher recovery of commercial components in copper-zinc ore dressing.*

**Key words:** copper-zinc ores, flotation, thermomechanical treatment, recovery, sphalerite, pyrite, steaming, attrition, regrinding, modernization.

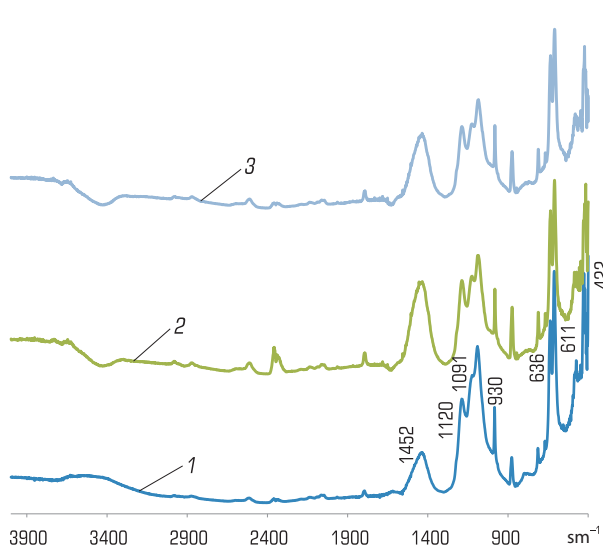
corded on IRAffinity-1 infrared spectrophotometer, DRS-8000, Shimadzu, in the wavenumber range 400–4000  $\text{cm}^{-1}$ , at a resolution of 4  $\text{cm}^{-1}$ , in the mode of diffusion.

The earlier X-ray electron spectroscopy analysis showed that on the surface of the initial specimens of sulfide, including sphalerite, sulfur atoms had at the least two signals — sulfide signal  $\text{S}^{2-}$  and sulfate signal  $\text{S}^{42-}$ , which implied the presence of zinc sulfides and sulfates on the surface [4–6].

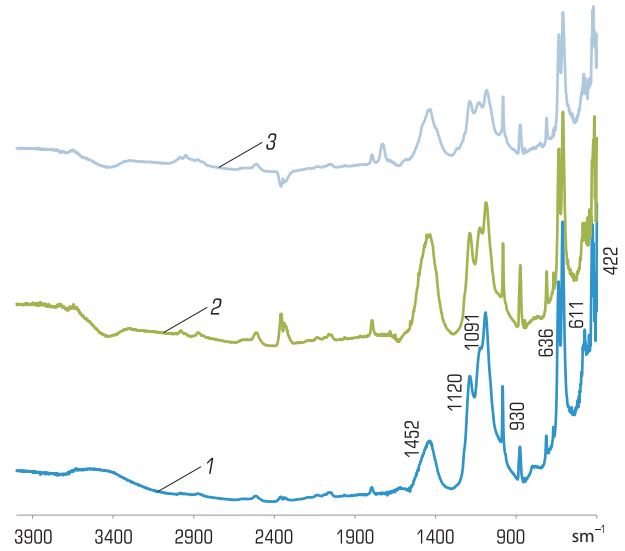
Therefore the influence of modification methods on the surface condition of sphalerite has been assessed based on the calculation of total area of absorption bands (AB) with the maximum within the spectral range (SR) 900–1300  $\text{cm}^{-1}$ , which conforms with the valence vibration of sulfate-ion, and with the maximum at 1450  $\text{cm}^{-1}$ , which conforms with the valence vibration of carbonate-ion (SR 1300–1600  $\text{cm}^{-1}$ ). The

The infrared spectroscopy research has been carried out by M. V. Ryazantseva, Candidate of Engineering Sciences (IPKON RAS).

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**Fig. 1. Infrared spectra of sphalerite surface:**  
 1 — initial specimen; 2 — after stirring in water medium;  
 3 — after steaming



**Fig. 2. Infrared spectra of sphalerite surface:**  
 1 — initial specimen; 2 — after stirring in water medium;  
 3 — after attrition

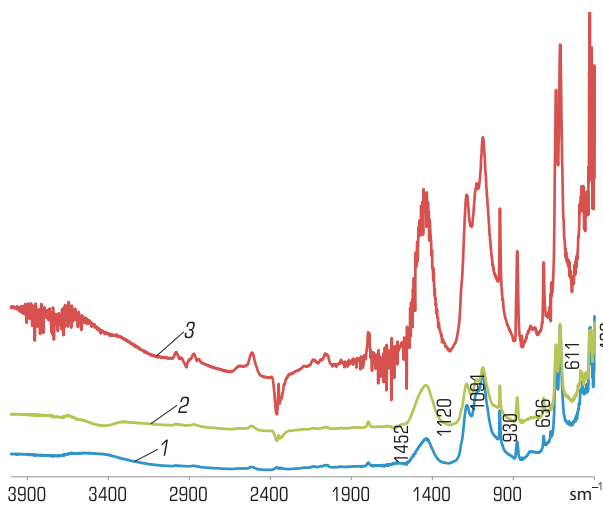
**Table 1. Frequency bias of surface compounds**

Modification of sphalerite surface	Shift of areas of bands fitting with deformation-induced fluctuations	
	Sulfate-ions (900–1300 cm <sup>-1</sup> )	Carbonate-ions (1442 cm <sup>-1</sup> )
Initial specimen	42.26	9.85
Stirring in water medium	38.19	25.63
Steaming	32.37	18.97
Attrition	21.04	11.15
Regrinding	123.74	63.7
Regrinding + attrition	46.53	26.79
Regrinding + attrition + steaming	46.87	29.19

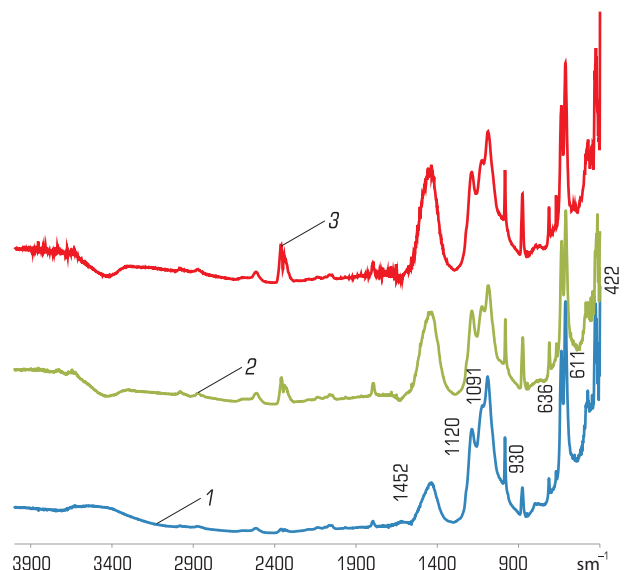
comparative analysis of the finite spectrum was carried out on a specimen after stirring in a water medium for 60 min — duration of flotation pulp run from milling to zinc flotation cycle, and after heat conditioning (steaming).

It has been found for sphalerite that stirring of initial sphalerite specimen in water medium for 60 min increases oxidation of its surface, which follows from 2.6 times growth of SR area with the maximum at 1400 cm<sup>-1</sup> (accumulation of carbonates) and 1.4 times growth of AB area with the maximum within 900–1300 cm<sup>-1</sup> (accumulation of sulfates) as seen in **Fig. 1** and from **Table 1**.

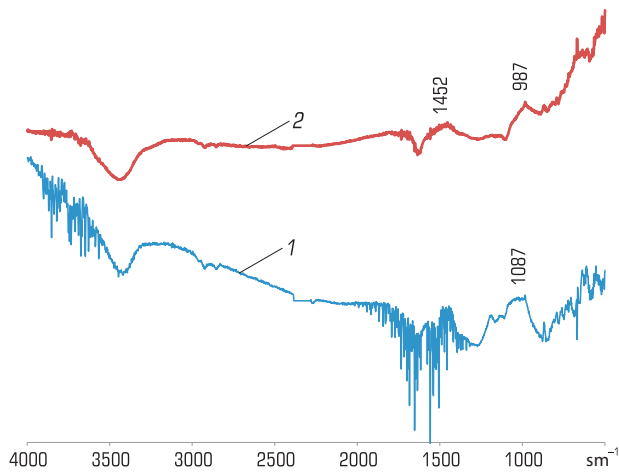
Steaming contributes to removal of unsolvable zinc carbonates from sphalerite surface and to reduction of sulfates, which is confirmed by decrease in the area of AB of the characteristic frequencies of sulfate-ions and carbonate-ions



**Fig. 3. Infrared spectra of sphalerite surface:**  
 1 — initial specimen; 2 — after stirring in water medium;  
 3 — after regrinding



**Fig. 4. Infrared spectra of sphalerite surface:**  
 1 — initial specimen; 2 — after stirring in water medium;  
 3 — after mechanical treatment package



**Fig. 5. Infrared spectra of pyrite surface:**  
1 — initial specimen; 2 — after attrition

1.4 and 1.2 times, respectively (refer to Fig. 1). The infrared spectroscopy has displayed the change in the composition of the surface compounds on the separated minerals with attrition, including the decrease in the amount of sulfates, carbonates and hydroxides and, consequently, the increase in the amount of sulfides, which follows from the reduction of areas of the characteristic AB of sulfate-ions and carbonate-ions 2.4–2.7 times (Fig. 2).

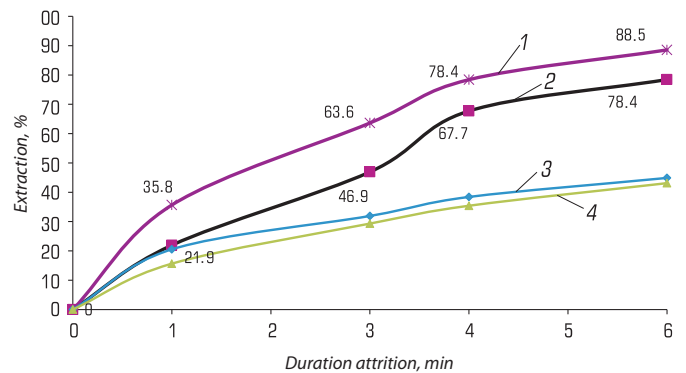
Considering the small-crystal structure of copper–zinc ores and very fine intergrowth of copper and zinc minerals, as well as pyrite, selective flotation is intensified by introduction of regrinding stage in the process charts, including the zinc cycle. For the purpose of estimating effect of regrinding on sphalerite surface, infrared spectra of initial sphalerite after stirring in water medium for 60 min and after regrinding have been recorded (Fig. 3). Regrinding greatly influences the condition of the compounds in the mineral surface layer: oxide forms arise again, which is confirmed by the growth of the area of AB fitting with fluctuations of groups  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$ .

Combination of regrinding and attrition of a test specimen results in reduction of AB conforming with valence vibrations of sulfate-ions and carbonate-ions, which indicates the reduction of the both in the surface layer 2.7 and 2.4 times, respectively.

Combination of three operations (regrinding + steaming + attrition) also reduces the amount of sulfates in the mineral surface layer, and the area of AB fitting with deformation-induced fluctuations of sulfate-ions and carbonate-ions lowers more than 2 times (Fig. 4).

It has been found that attrition of pyrite contributes to removal of sulfates and generation of ferric oxides, which implies that the spectrum of the mineral after attrition contains no wide AB with the maximum at  $1000\text{ cm}^{-1}$ , related with the valence vibrations of sulfate-ions, but contains a new band at  $987\text{ cm}^{-1}$  and a weak maximum at  $3600\text{ cm}^{-1}$ , which characterize fluctuations of Fe–O and O–H bonds, respectively (Fig. 5).

Fig. 6 presents the data on floatability of sulfides with and without mechanical treatment in water medium.



**Fig. 6. Recovery of sphalerite (1, 2) and pyrite (3, 4) depending upon their preparation for flotation:**  
2, 3 — without attrition; 1, 4 — with attrition

After attrition for 3 min, extraction of sphalerite grows by 17% and pyrite extraction lowers by 5%.

From the analysis of heat and mechanical influence on monomineral surface, it follows that:

- as sphalerite goes from milling to zinc flotation cycle, both carbonates and zinc sulfates accumulate on its surface;
- attrition reduces amount of sulfates, carbonates and hydroxides, and, consequently, increases amount of sulfides on the surface of sphalerite; as for pyrite, attrition greatly increases amount of ferric oxides promoting hydrophilization of the mineral, which can make flotation acidities of these minerals different;
- thermal treatment also reduces amount of carbonates and sulfates on the surface of sphalerite;
- regrinding significantly affects the composition of the compounds in the mineral surface layer: oxide forms of their elements generate again;
- combination of three operations (regrinding + attrition + steaming) results in reduction in the amount of sulfates and carbonates in the surface layer of sphalerite, which improves floatability of sphalerite and worsens floatability of pyrite.

So, attrition of surface of sulfide minerals having similar process properties (sphalerite and pyrite) changes the composition of their surface compounds. It is assumable that the decrease in the amount of sulfates and carbonates on the surface of sphalerite contributes to stronger attachment of a collector owing to generation of low-soluble zinc sulfide xanthate, which ensures hydrophobization and flotation of sphalerite. More intensive growth of hydroxide compounds on the surface of pyrite causes its hydrophilization and worsens floatability [7].

Based on the found mechanisms, the studies have been undertaken in order to improve zinc concentrate quality in copper–zinc ore processing at Uchalinsky Mining-and-Processing Integrated Works. In focus were concentrates of zinc “heads” as they make up to 60% of the total zinc concentrate.

Within the studies, the following chart of process stages has been developed: regrinding up to 70% content of  $-20\text{ }\mu\text{m}$  size — attrition for 3–5 min — aerification (10 min) and oxidation–heat conditioning ( $35\text{--}40\text{ }^\circ\text{C}$ ).

**Table 2. Comparative closed flotation of copper–zinc ore using conventional and recommended modes**

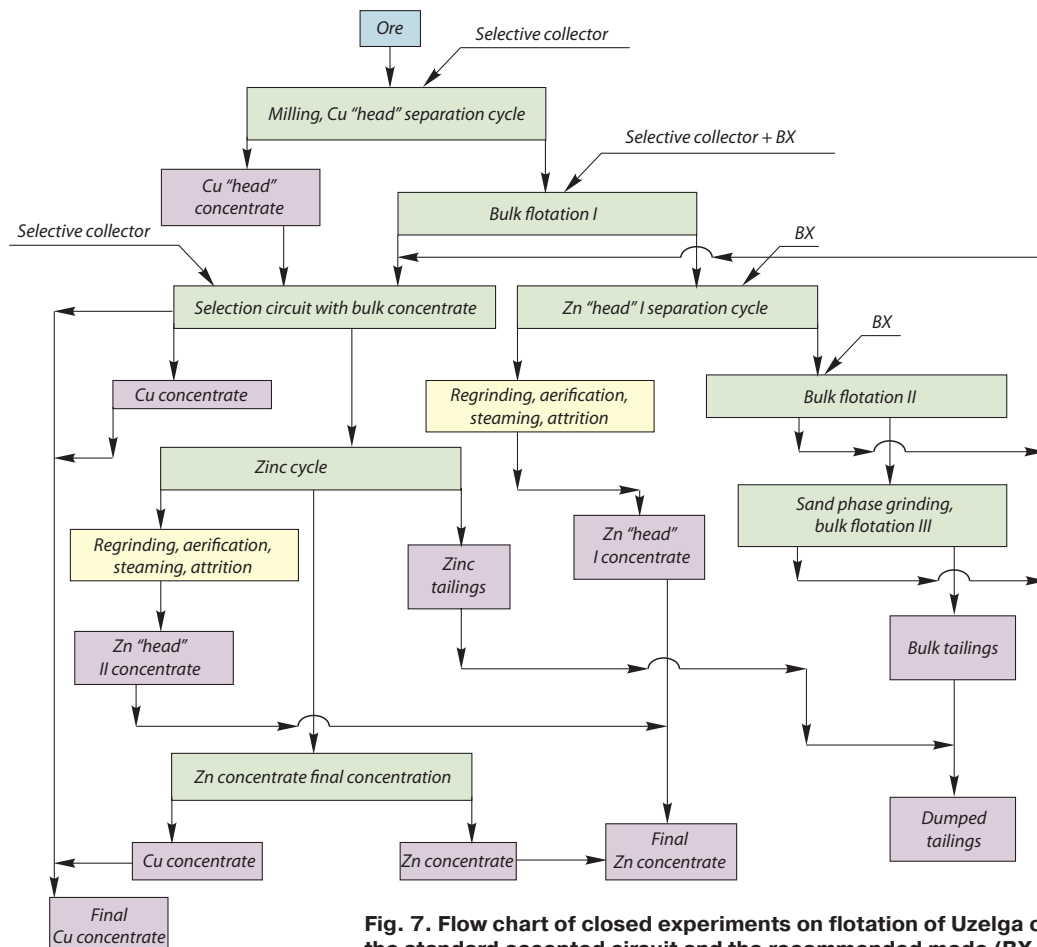
Product	Yield, %	Content, %		Recovery, %	
		Cu	Zn	Cu	Zn
<i>Conventional flotation chart</i>					
Cu concentrate	6.42	16.34	4.48	86.01	10.16
Zn “head” I	1.43	0.48	51.4	0.56	25.99
Zn “head” II	0.86	1.1	49.32	0.78	15.05
Zn concentrate for final concentration	2.23	0.75	47.34	1.37	37.27
Total Zn concentrate	4.52	0.73	49.03	2.71	78.31
Tailings	89.06	0.15	0.37	11.29	11.54
Ore	100	1.22	2.83	100	100
<i>Recommended flotation chart</i>					
Cu concentrate	5.09	20.67	3.41	86.2	6.2
Zn “head” I	1.55	0.4	52.01	0.51	28.77
Zn “head” II	1.65	1.1	53.5	1.49	31.48
Zn concentrate for final concentration	1.26	0.8	48.5	0.82	21.72
Total Zn concentrate	4.46	0.77	51.57	2.82	81.97
Tailings	90.46	0.15	0.37	10.99	11.82
Ore	100	1.22	2.8	100	100

**Table 2** compiles the data on flotation of pyritic copper–zinc ore from Uzelga deposit using the accepted flotation chart, with the combination of weak and strong collectors in the cycles of separation of copper “heads” and in bulk flotation I, and with the package of process stages of regrinding, attrition, aeration and steaming in the cycles of separation of concentrates of zinc “heads.” The closed flotation circuit with complete modeling of cycles of bulk, copper and zinc flotation and the cycle of final concentration of zinc concentrate is shown in the **Fig. 7**.

As seen in the figure, with the proposed flotation regime, the zinc concentrate amount in the zinc cycle grows from 49.03 to 51.57% at the same recovery.

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**Fig. 7. Flow chart of closed experiments on flotation of Uzelga copper–zinc ore using the standard accepted circuit and the recommended mode (BX — butyl xanthate)**

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## IMPROVEMENT OF FLOTATION TECHNOLOGY FOR RE-TREATMENT OF MAGNETITE CONCENTRATES



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At the present time when high-grade iron ore reserves are depleted and the world markets of iron ore materials face high competition, the quality standards for iron concentrates continuously grow. Iron ore producers have to modernize flow charts they use.

This is conditioned by advisable use of rich concentrates both in blast-furnace practices and in steelmaking, and by strict requirements imposed on the contents of iron, silica, toxic admixtures and moisture of the concentrates employed in direct reduction processes. The optimal content of iron and admixtures of concentrate is determined based on the comprehensive economic analysis of smelting and dressing performance indicators in the aggregate.

Currently, the routine method of increasing iron content of magnetite concentrates is their re-grinding and wet-type weak magnetic separation. Though readily available, this method yields minimum increment in iron content, consumes much energy and results in enlarged specific areas of concentrates, which has an adverse effect on moisture content of cake in filtration and pelletizing.

Currently, the most popular way of increasing iron content of magnetite concentrates is re-grinding and wet weak-magnetic field separation. Though readily available, this technology yields minimum increment in iron content, features high energy input and results in enlarged specific surface of concentrates, which has an adverse influence on moisture content of cake in filtration and subsequent pelletizing.

Flotation re-treatment of iron concentrates is technologically the most selective method of mineral processing, since it allows reduction of content of silica, phosphorus and other admixtures, and cardinally solves the problem on production of super concentrates.

At the present time when rich iron ore reserves have been depleted and the world market of iron ore material faces high competition, quality standards for iron concentrates increasingly grow. Iron ore producers have to modernize process flow charts they use.

Within the past ten years, RIVS Science and Production Association has accomplished a wide range of works toward improvement of iron ore processing technology and equipment (Russia, Ukraine, Philippines). The ample research has resulted in development of the technology for re-treatment of iron concentrates.

The paper describes the results obtained in re-treatment of magnetite concentrates by the method of reverse cationic flotation using collecting agents based on amines. High selectivity of the agents eliminates the use of depressors. Flotation uses hard water with partial water rotation. The re-treatment enables production of iron concentrates with the iron content of 69.5% (at the recovery of 94.62%) and silica content of 1.75%.

**Key words:** magnetite concentrates, aluminum silicate flotation, amines.

Perfection of iron concentrates in flotation is technologically the best selective method, since it allows reduction in content of silica, phosphorus, ash and other admixtures, and in a big way solves the problem of super concentrate production.