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SOME STUDIES ON UTILIZATION OF FLOTATION WASTES BY SPHERICAL AGGLOMERATION

A feasible technique for dewatering of thick suspensions of hydrophilic solids is described as applied to Pb-Zn and sulphur ores flotation wastes. The technique consists in treatment of flocullated wastes enabling the separation of the solid from the liquid on 1 mm or coarser sieves. Some parameters of the process and their influence on the form of the final product are discussed. Remarks referring to the design of an apparatus for continuous agglomeration are given. For the technique the terms "spherical agglomeration of flocculated precipitates" or "flocculation spherical agglomeration" have been proposed.

1. INTRODUCTION

Spherical agglomeration is a technique for separation of solid constituents from liquid suspension consisting in addition of a second liquid immiscible with the dispersing liquid and wetting preferably the solid. Some modifying agents which adsorb strongly at the solid particles and enhance the affinity of their surface towards the second liquid can be also added. As the second liquid a nonpolar liquid hydrocarbon — usually termed as "bridging" or "binding" liquid and as the modifier a long chain fatty acid may be used in case of water suspension. For suspensions in organic liquid (e. g. in CCl_4) this second liquid is just water which is a good binding agent, and as a modifier methyl alcohol or acetone may be used. When all the necessary agents are added the suspension must be stirred vigorously to distribute the agents on solid particles surface. After a few minutes of stirring the solid particles begin to aggregate forming hard spheres of several milimeters in diameter. The spheres can be readily separated from the mother liquid characterized by a pretty good clarity, using a sieve with comparatively coarse meshes.

Spherical agglomeration was first noticed by STOCK [1], and then explained qualitatively by PUDDINGTON et al. [2, 3]. Since then, the process has been widely applied as an

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aggregation [4] and dewatering [5, 6] technique in mineral dressing and coal industries. In spite of the lack of theoretical background for the process, a considerable progress seems to have been achieved lately by using flocculating agents instead of bridging liquid [7–9]. This procedure and the fact that the apparatus for a continuous process is known enables dewatering of large masses of suspensions of hydrophilic solids — e. g. water suspensions of gangue obtained in ore dressing. Because of the necessity of water reuse in ore dressing plants, the above technique seems to be of a growing importance.

Industrial wastewater is commonly clarified by flocculation followed by sedimentation or filtration [11–13].

This method is especially effective for suspensions with low content of solid particles. The treatment of large masses of wastewater with a high solid particles content require the usage of sedimentation pools of large area or filtration technique which are rather expensive. If a suspension containing about 20% of solids is treated by flocculant the final volume of flocculated precipitate is nearly equal to the initial volume of the suspension and no sedimentation is observed [14]. Thus the dewatering of such suspensions can be done by centrifugation.

On account of the situation depicted above the sperical agglomeration seems to be the most feasible and the cheapest technique for dewatering of large masses of wastes coming from flotation mills which in most instances have a form of thick aqueous suspension of gangue slimes. Solid product of spherical agglomeration process is easily stored in a form of waste-heap, and the water separated can be readily prepared for recycling. Some flotation wastes, moreover, e. g. sulphur flotation waste can be used in agriculture as a fertilizer. According to the recent opinion [15–18] the flocculants will be widely used as soil structuring agents approximately in the next decade. Thus, the spherical agglomeration technique seems to be promising for dewatering of flotation wastes since the product of the process may be obtained in form of granules of desired size. Such fertilizers containing a floculation agent, apart from limestone and bentonites, will be particularly valuable.

Preliminary work on application of the spherical agglomeration technique allowing the utilization of sulphur flotation wastes is described elsewhere [8, 9]. Further studies described in the paper have been compared with some results on agglomeration of wastes from Polish zinc-lead ores flotation. A pilot-scale apparatus for continuous agglomeration is presented in the Appendix.

2. EXPERIMENTAL

2.1. MATERIALS

Wastes from flotation of sulphur and zinc-lead ores were kindly supplied by "Siarkopol" Tarnobrzeg and "Bolesław", Bukowno near Olkusz, respectively. All the flocculants used (see table 1) were kindly supplied by the Manufacturers.

Table 1

Agglomeration effectiveness of some flocculants

Flocculant	Manufacturer	Composition	Type	Form of flocs	Test
Magnafloc 139	Allied Colloids Ltd, England	PAM	anionic	*g*—*s*	—
Magnafloc 155	,,	,,	,,	*s*	++
Magnafloc 156	,,	,,	,,	*s*	+
Rokrysol WF-2	NZPO „Rokita", Poland	6% PAM	,,	*g*—*s*	—
Primafloc A-10	Leming Chemical Ltd	20% PAM	,,	*g*	—
Gigtar	ZA Tarnów, Poland	6% PAM	,,	*g*	—
Sedipur TF-2	BASF, West Germany	PAM	,,	*g*	—
Praestol 2935	Stockhausen Krefeld, West Germany	,,	,,	*s*	—
Magnafloc 140	Allied Colloids Ltd, England	,,	cationic	*s*	—
Magnafloc 292	,,	,,	,,	*s*	—
Magnafloc 352	,,	,,	,,	*s*	+++
Magnafloc 455	,,	,,	,,	*s*	+++
Rokrysol WF-3	NZPO „Rokita", Poland	6% PAM	,,	*g*—*s*	+—
Magnafloc 351	Allied Colloids Ltd, England	PAM	nonionic	*s*	++++
Praestol 2900	Stockhausen, West Germany	,,	,,	*s*	—
Rokrysol WF-1 s	NZPO „Rokita", Poland	6% PAM	,,	*g*—*s*	++
Separan	Dow. Chemical Comp., USA	PAM	,,	*g*	—

PAM — polyacryloamide

2.2. METHODS

To substitute the bridging liquid by a flocculating agents a considerable modification of the spherical agglomeration process conditions is required. Instead of vigorous stirring, the suspension should be agitated or shaked gently so that the aggregates of flocculated precipitate undergo a continuous tumbling, impacting and ricocheting action against rounded surfaces. This can be easily achieved by rotation of the flocculated suspension in a horizontal drum with rounded protrusions on its internal walls formed parallelly to the axis of the drum. The rotation frequency should be carefully chosen since at too low frequency no agglomeration effects are observed and if it is too high the destruction of the agglomerates takes place. The units for batch [7] and continuous [10] agglomeration processes are sketched in figs. 1. and fig. 2, respectivelly. The inclined drum for continuous process has on its internal wall a helix to transport the agglomerates to the outlet. Suspension with an appropriate dose of flocculant is introduced by a tubing *f* [fig. 2) into inclined cylindrical drum (*a*) rotating with the chosen frequency. The flocculated precipitate experiences a tumbling and ricocheting action on the protrusions (*b*) inside the drum and is transported slowly by the helix (*c*) to the outlet of the drum (*a*). Both the pitch of the

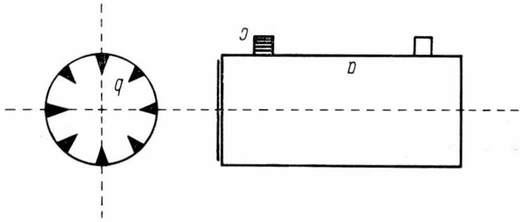

Fig. 1. Apparatus for batch flocculation spherical agglomeration

a) drum, b) protrusions, c) driving gear

Rys. 1. Aparatura do dozowania kulisto-kłaczkowej aglomeracji

a) bęben, b) występy, c) mechanizm napędowy

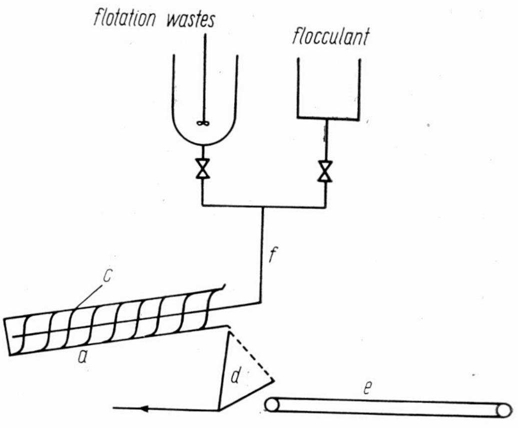

Fig. 2. Apparatus for continuous flocculation spherical agglomeration

a) inclined cylindrical drum, b) protrusions, c) helix, d) sieve, e) belt conveyor, f) suspension+flocculant inlet

Rys. 2. Aparatura do ciągłej kulisto-kłaczkowej aglomeracji

a) nachylony bęben cylindryczny, b) występy, c) spirale, d) sito, e) taśmociąg, f) otwór wlotowy dla zawiesiny i flokulanta

helix and the rotation frequency should be chosen to allow the formation of spherical agglomerates before the materials leave the drum. The agglomerated precipitate being separated from the mother liquid on an inclined sieve of coarse meshes, is given on a belt conveyor to be transported to a desired place. If necessary the aggregates may be dried on the conveyor with hot air. For all solutions municipal water was used. The pH and ionic composition of the suspensions were not modified during the experiments.

2.3. RESULTS AND DISCUSSION

It is obvious intuitively that there must exist a lower limit of strength of interparticle bonds formed by a flocculant, indispensable for spherical agglomeration to be formed.

In the first stage of agglomeration process, the flocs experience some destructive action and they have to be stable enough to be left unbroken. Thus, flocculation spherical agglomeration process requires the flocculants with relatively high floccualation effectiveness, and the doses — expressed per dry precipitate weight unit — considerably higher than those used for flocculation. On the other hand the upper limits of flocculant doses used are determined by the viscosity of flocculant solutions in higher concentrations since no agglomeration occurs if the viscisity of mother liquid is too high. Hence, the effectiveness of some flocculants is so low that the spherical agglomeration cannot be assured even by the highest possible concentrations. The flocculant chosen experimentally should be characterized by a high flocculation effectiveness, like e.g. Magnaflocs or Rokrysols. The corresponding results are presented in table 1. Tests were carried out at doses being reasonable for most active flocculant (marked by pluses in the table), and the highest possible for the others. Since the usefulness of a flocullant agglomeration can be forseen by an experienced experimenter from the form of flocs, the table contains also some observations in this respect. Two forms of flocs were distinguished for that purpose: the grained (*g*) and structural (*s*) ones. As can be seen from table 1 the structural form of flocs is a favourable symptom as far as the agglomeration is concerned. The estimation of the agglomeration quality is an approximate one. Four pluses assigned to the product (table 1) mean that it has a highly spherical form and that its resistance against mechanical action is high enough to be shovelled. The water content of such agglomerates is nearly one half of that of flocculated material. They can be easily separated from clear mother liquid on sieves of coarse meshes. The agglomerates marked with only one plus are much smaller, easy to deform or destroy, and the mother liquid after separation on 0.1 mm sieve is not quite clear. Nevertheless, the product can be formed in a heap of slope of about 45°. It have to be pointed out, however, that all the products of spherical agglomeration process, including that signed with"—+" mark, can be additionally dewatered by drying on the belt conveyor, and then granulated by one of the well-know techniques [4]. The additional drying treatment is only the matter of economics.

The form and size of spherical agglomeration product are controlled by the kind and dose of the flocculant used (fig. 3 and photograms in fig. 4). The curves representing the distribution of spherical agglomeration size depending on various doses of four flocculants may be used to choose both the appropriate flocculant and its dose. From the comparison of the curves in fig. 3 it may be inferred that agglomeration process depends also on the material. If the satisfactory diameter of the granules ranges within 1–2 mm, then Magnafloc seems to be a good reagent for Zn-Pb flotation wastes at doses as low as 100 g per ton of the solid wastes. This flocculant can be also used for agglomeration of sulphur flotation wastes, though two others, i.e. Magnafloc 352 and 455 gave equally good results at the same doses. It appears that for agglomeration of sulphur flotation wastes the minimal doses of the flocculant are 2.5 times higher than those for Zn-Pb. As it follows from fig. 3, for hugner doses of flocculants the size homogeneity of the spherical agglomerates is higher (see fig. 3a, e, f, d), and it decreases with the increasing amounts of flocculants, at the same time the average diameter of the agglomerates considerably increases. Some additional information on the dependence of the agglomeration form on the kind and dose of the flocculants are given by the photograms presen-

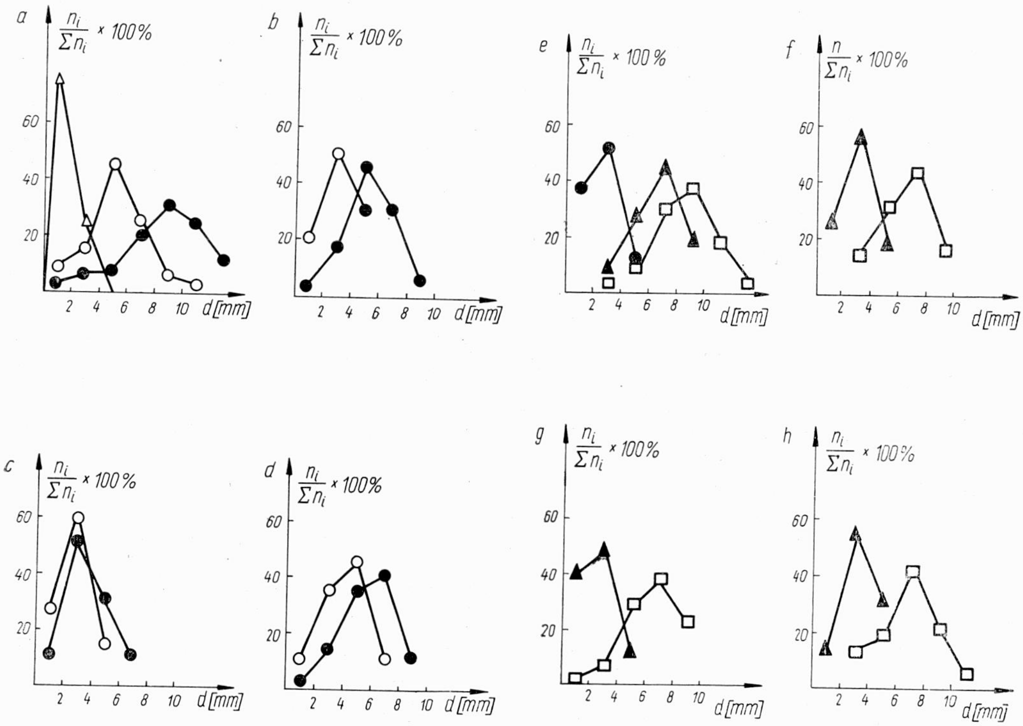

Fig. 3. Experimental size distribution of spherical agglomerates obtained under various conditions

Frequency — 20 rpm, rotation time — 3 min

a, b, c, d — Zn—Pb flotation wastes, Magnafloc 351, 352, 155, and 455, respectively

e, f, g. h — sulphur flotation wastes, Magnafloc 351, 352, and 455, respectively

△ — 100 grams of flocculants per ton of solid

○ — 200 ,, ,, ,, ,, ,, ,, ,,

● — 300 ,, ,, ,, ,, ,, ,, ,,

▲ — 500 ,, ,, ,, ,, ,, ,, ,,

□ — 800 ,, ,, ,, ,, ,, ,, ,,

Rys. 3. Eksperymentalny rozkład wielkości kulistych aglomeratów otrzymanych w różnych warunkach

Częstotliwość 20 obrotów/min., czas doświadczenia 3 min

a, b, c, d — odpady poflotacyjne Zn—Pb; e, f, g, h — odpady poflotacyjne siarki, Magnafloc odpowiednio 351, 352, 155 i 455

ted in fig. 4. In general, from figs. 3 and 4, it may be inferred that as far as the two materials studied are concerned, the agglomerates of a desired form may be obtained in a rather wide range by the right choice of the flocculant and its dose. The dependences of the water content and stability of agglomerates (which in some way are interrelated) on the flocculant dose and time of rotation are presented in table 2. It is seen that the decrease in water content due to prolongation of the rotation time was achieved only for higher doses of the flocculants. If lower doses of the flocculant were applied the prolongation of the rotation resulted in destruction of the agglomerates. In mother liquid the content of the flocculant used were rather negligible. As an example the concentrations of Magnafloc 351 determined by turbidimetry [9] are given in table 3. All the flocculation tests of mother liquid, with flocculant doses up to 800 g per one ton of solids gave negative results. Thus, wastewater treated by agglomeration technique may be re-used directly.

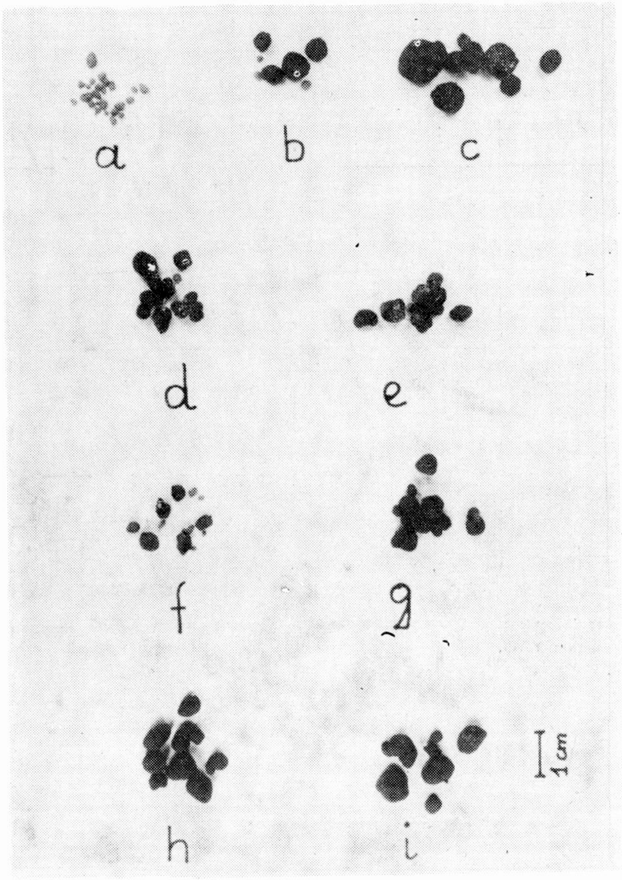

Fig. 4. Photograms of spherical agglomerates of Zn-Pb flotation wastes obtained under various conditions

Frequency — 20 rpm, rotation time — 3 min
a — 100 grams of flocculant per ton of solid — Magnafloc 351
b, d, f, h — 200 grams of flocculant per ton of solid — Magnafloc 351, 352, 155, 455, respectively
c, e, g, i — 300 grams of flocculant per ton of solid — Magnafloc 351, 352, 151 and 455, respectively

Rys. 4. Fotogramy kulistych aglomeratów odpadów poflotacyjnych Zn-Pb, otrzymanych w różnych warunkach

Częstotliwość 20 obrotów/min, czas doświadczenia 3 min.

Table 2

Water content and stability of the agglomerates of Zn-Pb flotation wastes (frequency = 20 rpm)

Flocculant	Dose/g (t)	Rotation time (min.) 3	6	9
		water content (%)		
MF-155	200	+ 38	destr 40	
	300	+ 41	destr 40	
MF-351	100	+ 36	+ 34	destr 36
	200	+ 36	+ 34	+ 32
	300	+ 36	+ 35	+ 33
MF-352	200	+ 36	+ 34	destr 35
	300	+ 36	+ 34	destr 34
MF-455	200	+ 36	+ 35	destr —
	300	+ 33	+ 33	destr —

„+" — good quality of the agglomerates,
„—" — bad quality of the agglomerates,
destr. — partial destruction.

Table 3

Content of Magnafloc 351 in water separated from the agglomerates

Dose g/Mg	Flocculant concentration in water separated from agglomerates g/dm^3 sulphur flotation wastes	Zn-Pb flotation wastes
100	—	10^{-5}
200	—	4×10^{-5}
300	10^{-5}	2×10^{-4}
500	5×10^{-4}	—
800	1.5×10^{-3}	—

2.4. CONCLUSIONS

1. Feasibility of dewatering of Zn-Pb and sulphur flotation wastes by flocculation spherical agglomeration technique was proved. Flocculants for the process were selected from the reagents available in our laboratory.

2. Form of the product obtained by this technique is ready to control by changing the frequency and rotation time, as well as the kind, and dose of flocculant. It may be expected that pH and ionic composition of the suspension may affect the agglomeration process; the effect of these parameters being difficult to change in case of huge masses of flotation wastes have not been studied in this work.

3. Solid product of agglomeration process can be readily stored in waste-heaps or, if desired, may be submitted to further drying and granulation.

4. In general, water separated from the spherical agglomerates contains negligible concentrations of the flocculant used. It can be directly recycled, provided that harmful admixtures are not present.

So far, there is a lack of more comprehensive treatment of the spherical agglomeration technique, either oleic or flocculation, and it is understood only qualitatively. Like all the papers concerned with the technique, the present one is only an attempt to solve a practical problem. The need for studies on the physicochemical basis of spherical agglomeration is, however, quite apparent.

APPENDIX

SOME REMARKS ON DESIGN OF APPARATUS FOR CONTINUOUS SPHERICAL AGGLOMERATION OF FLOCCULATED PRECIPITATES

As far as the process alone is concerned the following preliminary assumptions may be taken arbitrarily:

- ratio of the diameter of the drum to its length may vary from 2 to, say, 0.1,
- pitch of the internal helix may vary from several to tens of centimetres,
- height of the helix may range between 0.1 to 0.9 radius of the drum,
- height of the internal protrusions may range between 1 to 10 cm, and distances between them from several to tens of centimeters, and so on.

While choosing the quantities such factors as durability of the materials used, ease of operation and so on should be taken into acount. It is obvious that if only one of the parameters is chosen then the others have to be fitted to it. Such factor as optimum linear velocity of the wall of the drum and the optimum time of rotation (time of transport of the agglomerated material from lower to the upper part of the drum) are to be found experimentally for the material treated, and consistent with all the primary assumptions. An experimental unit of the efficiency of 200–400 kg per metric ton was constructed in our laboratory. The main dimensions of the unit are (see fig. 2):

- 30 cm in diameter and 150 cm in length,
- pitch and height of the helix 15 cm and 10 cm, respectively,
- height of the protrusions — 8 mm, a space between them — 10 cm.

Rotation frequency of the drum may be changed continuously from 6 to 15 per minute.

The choice of parameters was based on results from the tests: flocculation, agglomeration, and helix transport occurring during the whole agglomeration process. To facilitate visual observation of the process the drum was made of plexiglas.

The data obtained from tests were used to design another apparatus of the efficiency of 10 tonn per hour.

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BADANIA NAD WYKORZYSTANIEM ODPADÓW POFLOTACYJNYCH PRZY ZASTOSOWANIU AGLOMERACJI SFERYCZNEJ

Opisano prostą metodę odwadniania gęstych zawiesin hydrofilnych osadów oraz jej zastosowanie do odpadów z flotacji rud Pb-Zn i siarki. Metoda polega na hydromechanicznej obróbce sflokulowanych osadów, która umożliwia oddzielenie składników stałych od cieczy na sicie o oczkach 1 mm lub większych. Przedyskutowano parametry procesu i ich wpływ na postać produktu końcowego. Podano praktyczne wskazówki do projektowania urządzenia pracującego w układzie ciągłym. Dla opisanej metody zaproponowano termin "aglomeracja sferyczna sflokulowanych osadów" lub "flokulacyjna aglomeracja sferyczna".

TRENNUNG UND VERWERTUNG VON FLOTATIONSRÜCKSTÄNDEN MITTELS SPHERISCHER AGGLOMERIERUNG

Eine recht einfache Methode der Entwässerung von Grobstoffen hydrophiler Schlämme sowie deren Anwendung zur Entwässerung von Flotationsrückständen der Pb- und Zn-Erze wie auch des Schwefels wird erläutert. Die Methode beruht auf hydromechanischer Aufbereitung der Flockenschlämme und einer nachfolgenden Abtrennung der Feststoffe auf einem Grobsieb mit Maschenweiten $\geqslant 1$ mm. Diskutiert werden die Prozessfaktoren und deren Einfluß auf die Form des Endproduktes. Gegeben sind praktische Hinweise für die Projektierung einer kontinuierlich arbeitenden Anlage.

Für die beschriebene Methode wird der Name "spherische Agglomerierung flockiger Schlämme" bzw. "spherische Flockungs-Agglomerierung" vorgeschlagen.

НЕКОТОРЫЕ ИССЛЕДОВАНИЯ ПО УТИЛИЗАЦИИ ФЛОТАЦИОННЫХ ОСТАТКОВ С ПОМОЩЬЮ СФЕРИЧЕСКОЙ АГЛОМЕРАЦИИ

Описан простой метод дегидратации плотно взвешенных гидрофильных осадков, а также его применение к отходам флотации Pb-Zn сернистых руд. Метод основан на гидромеханической обработке сфокулированных осадков, которая позволяет в дальнейшем отделить твердые компоненты от жидкости на сите с отверстиями I мм или больше. Обсуждены параметры процесса и их влияние на вид конечного продукта. Даны практические рекомендации для проектирования оборудования, работающего в непрерывном процессе. Для описанного метода предложен термин ,,сферическая агломерация сфокулированных осадков" или ,,фокуляцийная сферическая агломерация".

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