View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by Electronic archive of Tomsk Polytechnic University

Available online at www.sciencedirect.com
ScienceDirect
Procedia Chemistry 10 (2014) 305 – 309
Procedia Chemistry

XV International Scientific Conference "Chemistry and Chemical Engineering in XXI century" dedicated to Professor L.P. Kulyov

Using of the agglomeration-in-liquid for the technology of the fine materials

O.K. Semakina [a] *, S.A. Babenko [a], N.V. Vakhrameeva [a]

[a] *National Research Tomsk Polytechnic University, 30 Lenin avenue, Tomsk 634050, Russia*

Abstract

The content of the fine and ultrafine particles in the raw material results in difficulty of the separation, the loss of the valuable components and ecological contamination. Secondary using of the fine particles is impossible without their granulation. This problem has been solved by the agglomeration-in-liquid method.
An agglomeration-in-liquid method is a process to produce agglomerates in a liquid phase from solid particles suspended in the liquid. The surface of solid particles and the binding liquid must be of identical polarity, but the continuous phase must be of the opposite polarity. The water solutions of the surfactant are the binding liquids or the organic liquids.

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).
Peer-review under responsibility of Tomsk Polytechnic University

Keywords: agglomeration-in-liquid; sapropel; polymer particle; granule

1. Introduction

The content of the fine and ultrafine particles in the raw material results in difficulty of the separation, the loss of the valuable components and ecological contamination. Secondary using of the fine particles is impossible without their granulation. These problems have been solved by the agglomeration-in-liquid method.

The agglomeration-in-liquid method is a process to produce agglomerates in a liquid phase from solid particles suspended in the liquid. The surface of solid particles and the binding liquid must be of identical polarity, but the

* Corresponding author: Olga K. Semakina. Tel.: +7-960-973-0081.
E-mail address: nataliya@tpu.ru

1876-6196 © 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).
Peer-review under responsibility of Tomsk Polytechnic University
doi:10.1016/j.proche.2014.10.051

continuous phase must be of the opposite polarity. The water solutions of the surfactant or organic liquids are the binding liquids.

The surface properties of the solid particles are better developed on the liquid-liquid boundary, than on the gas-liquid boundary observed in the usual granulation methods: a rolling method on the granulator of a plate or drum type, an extrusion and a spray-type drying. The continuous liquid phase promotes the change of the physical-chemical properties of the surface of solid particles. Thus the granules can be obtained from the fine solid particles with the polar and non-polar surface by the agglomeration-in-liquid method.

An agglomeration-in-liquid method has been widely used at enterprises that deal with the processing of dispersed materials: selective granulation of gold particles[1-4]; the extraction of valuable minerals from ore pulps[5]; soot-water suspension separation[6-7]; oil granulation in coal enrichment technology[8-13]; separation of fine-grained ore minerals[14-18], etc.

2. Experimental

In this work there are results of the granulation investigation of the fine polymer particles, the spherical catalysts, the carbon particles, the carbon fibers and the complex fertilizer.

The agglomeration-in-liquid method depends on physical-chemical and hydrodynamic factors. The physical-chemical factors are properties of the surface of solid particles and density and tenacity of entire and discrete liquid phases.

According to the difference in mechanism of generating the cohesive force the agglomeration-in-liquid method is classified into two methods. In the first method an immiscible second liquid called bridging liquid is used. In the second method the organic flocculants of high molecular weight is used.

We considered the process of agglomeration-in-liquid produced by the first method. Production of the fine spherical catalyst granules consists of the following stages:

the first – suspending the polar catalyst powder in unpolar liquid;
the second – dispersion of the polar bridging liquid;
the third – hydrodynamic influence by mixing or shaking;
the fourth – the formation of the agglomerates from solid particles and drops of bridging liquid;
the fifth – growth and densification of granules.

Cohesion of solid particles on the surface of drop is a primary period of the agglomeration-in-liquid method. Then solid particles are wetted by bridging liquid and penetrate into drops by surface tension. Distribution of the bridging liquid in the aggregates is classified into three states, namely, pendular, funicular and capillary.

Tensile strength of the aggregate depends upon the following factors related to the above mentioned state: porosity of aggregate, interfacial tension, contact angle, amount of bridging liquid, particle size, etc. When an excess amount of the bridging liquid is added, the particles transfer to the bridging liquid phase. If particles have medium wettability to the bridging liquid, emulsion would be formed. If the other solid particles which are unwettable to the bridging liquid exist in the system, the particles remain in the entire liquid phase as suspension in all of the cases.

The necessary condition for the agglomerate formation is that the angle across bridging liquid must be between 0^o and 90^o. The hydrophobic degree of the catalyst particles and the interfacial tension are regulated by addition of the modifier to the suspension or treatment of the powder surface. Usually ethanol is used for treatment of the surface of the catalyst particles.

General index of estimation of a dispersed material ability to the agglomeration-in-liquid method – *IG* – is presented:

$$IG = \frac{V_1 - V_2}{V_{\max}}$$

where V_1 – the specific sediment volume of sediment of solid particles in non-polar medium, cm^3/g;
V_2 – the specific sediment volume of sediment of solid particles in polar (water) medium, cm^3/g;
V_{max} – the maximum sediment volume of sediment of solid particles, cm^3/g.

Magnitude of the *IG* varies in the range of –1 to +1. Solid particles with the *IG* = 0÷1 must be granulated in the non-polar medium and with the *IG* = 0 ÷ –1 – in the polar medium.

Hence, many processes could be proposed according to the properties of aggregates which are sufficient for practical purposes.

In our investigation the solid particles are oxides of metals[19]. This is aluminum oxide, potassium oxide, silica, sodium oxide etc. As bridging liquid we use the solution of surfactants and the silicate sol of different concentration. The entire liquid phase is hydrocarbons, fluorocarbons and other organic liquids.

The agglomeration-in-liquid method is realized in the polymer shaking granulator or in the polymer vessel with an impeller mixer.

The size of granules depends on the impeller speed, quantity of components and the particle size. The density and tenacity of the bridging liquid and an entire liquid phase play the important role, too.

The spread of agglomerate sizes increases with decreasing the particle size. The sizes of granules decrease with increasing the impeller speed. It is important to point out that the density of the bridging liquid is less than the density of the entire phase. The density of solid particles is the more than the density of entire phase.

As our investigations showed the optimum conditions of the fine spherical catalyst production are following:

1) impeller speed is from 1000 to 1500 turns per minute;

2) the time of agglomeration is from one half till two minutes;

3) the relationship between the bridging liquid and the entire liquid phase is from 0.3 to 0.9 wt. %;

4) the ratio between the solid particles and the bridging liquids is from 3 to 12 wt. %.

Moreover the agglomeration-in-liquid method let us get the double layer granules of the catalyst[20]. The core of granules consists of the catalyst bearer. Usually it is silica or aluminum oxide. But the outside layer of granules consists of different metal oxides. The double layer granules are necessary when the catalytic reaction occurs on the outside layer of granules.

We investigated the kinetics of agglomeration of binary particle mixture in liquid suspension by immiscible liquid wetting. Particles alone exhibited a maximum when the fine particles were added to the coarse particles at the 10 to 30 wt. % level. This maximum rate of agglomeration is related to the packing properties of the binary particle mixtures. It occurs at the fine/coarse ratio with which the added bridging liquid occupies a maximum proportion of the internal voids of the agglomerates.

Selective granulation can be realized by the agglomeration-in-liquid method. Selective agglomeration is the merit of this method[21].

In this work there are results of investigation of the fine polymer particles granulation[22]. The granules from the polymer particles have been used as carrier. The agglomeration-in-liquid method of the polymer particles involves the next stages:

1) modification of the solid particles, selection of the optimum concentration of the modifier and time of treatment;

2) selection and preparation condition of the binding liquids;

3) compatibility of the fine particles with polar and non-polar surface in the granule;

4) measurement of the adhesion strength of the particles inside the granule;

5) determination of the optimum regime of the granulation (the solid : liquid phase relation, the binding consumption, the time of the granulation).

As the results showed the polymer granules are high efficient for the selective separation of the valuable minerals. The separation conditions are following:

1) the valuable mineral content in the waste is not more than 0.18 g/t;

2) the ratio of the continuous phase to solid particles is equal to 1 : 4;

3) the carrier has been taken from 0.8 to 1 wt. % towards a solid phase;

4) the agitation time of the suspension and the carrier is from 4 to 6 minutes.

Before addition of the carrier, the suspension has been treated by the reagents used in ore milling.

Recently late a great attention has been paid to the production of fertilizer with better physical and chemical properties. Future belongs to the fertilizer having a complex mixture and possessing a long-continued action, a dispersive structure and non-caking characteristics. These properties can be obtained by granulation. In this work there are results of investigation of complex fertilizer production on the basis of lake sapropels of the Tomsk region with phosphorite flour and mineral compositions. The mineral compositions consist of potassium salts, ammonium salts and their mixture. The sapropel content in granules has been taken from 1 to 35 wt. %.

Using of the lake sapropels considerably decreases dissolving of mineral salts from granules. The steady dissolving and a long-continued action of the fertilizer result in slow assimilation of the components by herb roots. It allows escaping a burning effect of roots. Decreased dissolving of the fertilizers prevents them from sluicing by rain and impedes the penetration in the surface waters.

The complex fertilizer granules on the basis of phosphorite flour have been prepared by agglomeration-in-liquid method[23]. In our investigations phosphorite flour is a polar substance; therefore a binding liquid may be any water-soluble potassium salt or ammonium salt, which is a component of complex fertilizers. The granulation is produced in the hydrocarbon liquid at the ratio of the continuous phase to binding liquid to solid particles equaled to 75–275 : 0.3–0.5 : 1.6–6 (wt.). The granulation time is two minutes.

The agglomeration-in-liquid method gives us a chance to produce simultaneously the non-caking complex fertilizer and completely eliminates the treatment stage of the obtained granules by anti-pressing powders. The complex fertilizer granules on the basis of lake sapropels and phosphorite flour have high strength, slow dissolubility and the long time effect.

The investigation the agglomeration-in-liquid process of carbon fibers has been carried out. The optimum regime of carbon fiber concentration in the water medium, the expense of the binding liquid and the agglomeration time are defined. The technological scheme of the carbon fibers agglomeration is recommended and tested. Ability of production of composite materials on the basic polymers and agglomerated carbon fiber base is determined. Using the carbon fibers as granules improves the working conditions and prevention of accidents, excepts discomfort of the transpose, measuring, etc., which gives ability to automate composite material production.

The results of the investigation of the mechanism carbon agglomeration from the liquid suspension and the determination of the optimum process conditions (expense of bonding liquid, S : L relation in the system, temperature, surfactant presence, a number of the shaft granulator rotation, etc.) allowed developing an effective process of the carbon-water suspension separation with simultaneous production carbon-fuel oil granules, which have a diameter from 2 to 4 mm and suitable properties developing as fuel.

3. Conclusion

Agglomeration-in-liquid of fine particles enables efficiently division of the heterogeneous systems and preparation of the granules from powders that meet the requirements of industry. The elementary stage of agglomeration-in-liquid process is the aggregate-complex formation that consists of drops of binder liquid and fine solid particles penetrated into it.

The generalized index to evaluate the granulation ability of dispersed particles was proposed. The granulation index (GI) is based on the change of sedimentation volume of the particle dispersed in liquid of opposite polarity.

The advantage of the agglomeration-in-liquid method is an ability to granulate the dispersed materials of various nature including materials that require pre-hydrophobization of particle surface. Gas replacement by liquid enables to more clearly show the surface properties of the agglomerated particles and to purposefully control the granulation process.

References

1. House I., Townsend I., Veal C. J. Coal gold agglomeration, *Int. Mining* 1988; **9**:17–19.
2. Bellamy SP, House CI, Veal CJ. Recovery of fine gold from a placer ore by coal gold agglomeration. *Proceedings of 1st Joint International Meeting between SME and Aus,* Littleton, 1989, 347–352.
3. Cadzow V, Lamb R. Carbad gold recovery, *Proceedings of 1st Joint International Meeting between SME and Aus*. Littleton, 1989, 375–379.
4. Beletsky VS, Elishevich AT. Adhesive method of extraction of gold from ores and scatterings, *Precious and rare metals*, Donetsk, 1994; **1**:25–26.
5. Rikhvanov LP, Kropanin SS, Babenko SA, et al. Zircon-ilmenite loose fields – as a potential source of development of the West Siberian region, Kemerovo, 2001.
6. Patent N 444919 Australia 23.01.74 Process for the separation of ash-forming components from an aqueous soot suspension. P. Visser, J.

van Den Berg Godfried.
7. Zuiderweg FJ, von Lookeren Campagne N. Pelletizing of Soot in Waste Water of Oil Gasification Plant-the Shell Pelletizing Separator (S.P.S.). *Chemical Engineering* 1969; **200**: 223–227.
8. Rao TC, Bandopadhyay P. Processing of Indian coal-fines, *Fine Particles Process: Proc. Int. Symp*., Las Vegas, 1980, 977–989.
9. Takacsi-Nagy Andras. A legfinomabb szeniszapok olajagglomeracios dusitasa, *Neherip. musz. egyet. kozl.*, 1982; **31** (3-4): 217–233.
10. Patent N 4416424 USA 22.11.83. Method and apparatus for deashing coal liquefaction effluents. Burke FP.
11. Ignasiak I., Carson D., Pawlak W. et al. Application of coal agglomeration for clean-up of hydrocarbon contaminated soil. *Int. Conf. Coal. Sci*., Tokyo, 1989; **2**:1019–1022.
12. Polwak W, Briker Y, Ignasiak B. Simultancous low-severity upgrading of subbituminous coals and heavy oil. *Int. Conf. Coal. Sci.*, Tokyo, 1980; **2**:1035–1038.
13. Powlak W, Szymocha K, Briker G. et. al. High-sulfur coal upgrading by improved oil agglomeration. *Proc. and Util. High-Sulfur Coals: 3rd Int. Conf., Ames, Iowa*, 1989, Amsterdam, 1990, 279–287.
14. Harada T, Matsuo T. Effects of feed size and surface property of minerals on agglomeration in water. Studied on the spherical agglomeration of sulphide minerals in water. *J. Mining and Met. Inst. Jap*, 1985; **1168**:369–374.
15. House CI, Veal CJ. Selective recovery of chalcopyrite by spherical agglomeration. *Miner. Eng.* 1989; **2**:171–184.
16. Gouri CN, Rao GV. Recovery of low grade scheelite by spherical agglomeration. *Miner and Met. Process.* 1990; **2**:79–83.
17. Dawwei W, Kewn W, Jicun Q. The activation mechanisms of wolframite by Ca^{+2} and Fe^{+3} ions in hydrophobic agglomeration, using sodium oleate as collector. *Inter. J. Miner. Process.* 1987; **2 (1-2)**:35–44.
18. Allen RP, Veal CJ. The spherical agglomeration of cassiterite. *Proc. 16th Int. Mines. Process. Congr.* Amsterdam, 1988, 1109–1120.
19. Inventor’s certificate N 1245336 USSR 22.03.96. Granulation method of oxide catalyst. Babenko SA, Mordvinova OK. et al.
20. Inventor’s certificate N 1771808 USSR 1.06.92. Granulation method of oxide-containing catalyst. Babenko SA, Semakina OK, Lakstrem I.V.
21. Patent N 2099146 RU 20.12.97. A method of extracting valuable minerals from the ore slimes. Babenko SA, Semakina OK, Graver V.S.
22. Patent N 2015144 RU 30.06.94. Granulation method filled polyolefin’s. Babenko SA, Semakina OK, Sidorenko AA.
23. Inventor’s certificate N 1567559 USSR 1.02.90. Granulation method of complex fertilizers. Babenko SA, Semakina OK.