Journal of Engineering Physics and Thermophysics, Vol. 77, No. 5, 2004

FEATURES OF HEAT TRANSFER IN THE GRANULATION OF SULFUR

N. V. Selivanov and P. V. Yakovlev

UDC 661.21.002.6

The influence of the temperature regimes of the granulation of sulfur in an aqueous medium on the qualitative characteristics of the granules obtained has been experimentally investigated. The admissible range of change in the operating parameters of an apparatus for granulation of sulfur with the use of water has been determined and a dimensionless quantity defining this range has been derived. The influence of the heat-transfer regimes on the formation of the internal structure of sulfur granules has been numerically investigated and the reasons for the dependence of the qualitative characteristics of the granules on the temperature conditions of their production have been revealed.

The tendency toward automatization of production processes and mechanization of transportation of loose materials have generated a need for the production of granular materials. The granulation of dusty materials makes it possible to solve problems of environmental protection. The granulation of sulfur has features determined by the physicochemical properties of this substance.

Sulfur granules should be produced in accordance with the requirements imposed on their size, strength, chemical composition, moisture content, etc. by the standards for marketable products [1]. The comprehensive analysis of the existing methods of production of granular sulfur made in [2] has shown that each of these methods has its own advantages and disadvantages.

There are various methods of granulation of sulfur, in which the melt is cooled in different ways. In apparatus for granulation with the use of air cooling, for example, by the Procor or Ciech methods [3], the melt drops are cooled in an air flow. These apparatus represent towers with an ascending air flow. Apparatus for granulation of sulfur with the use of air make it possible to obtain high-quality granules; however, they are expensive and a large amount of sulfur is carried away from them by the outward air flow, which pollutes the environment. There is a method of production of granules in fluidized-bed apparatus [3]. However, apparatus for granulation of sulfur in a fluidized bed have not received wide acceptance because of their explosion hazard. Sulfur granules can be obtained by solidification of melted sulfur drops on a cooled surface. Such granules have an irregular shape and their transportation is accompanied by the formation of a large amount of dust.

In apparatus for granulation of sulfur by water, the sulfur melt is cooled in a water flow. The main disadvantage of this method is the high content of moisture in the granules obtained and the dependence of their shape and strength on the technology realized. At the same time, this method has received wide acceptance because granulation of sulfur with the use of water is safe for the environment and apparatus in which this process is realized are highly productive.

Beginning with the first (Elliot) apparatus for granulation of sulfur by water [3], the desired quality of the product obtained was provided by slowing-down the process of heat transfer and keeping granules from sticking together with the use of surface-active elements.

As a result of our investigations, we have obtained the dependence of the main qualitative characteristics of granulation products on the heat-transfer processes in them, using which, one can obtain a high-quality product by changing the temperature conditions of cooling the melt drops without recourse to additions. This method can be realized in apparatus for granulation of sulfur, whose design is described in patents [4–6].

Astrakhan' State University, 16 Tatishchev Str., Astrakhan', 414025, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 77, No. 5, pp. 29–34, September–October, 2004. Original article submitted April 15, 2003; revision submitted February 19, 2004.

 1062-0125/04/7705-0904

The object of our investigation is a sulfur drop. Since this object is small in size and is moved and cooled rapidly, we will investigate it by a complex method theoretically with the use of a numerical model describing the internal processes and experimentally with the aim of obtaining the integral characteristics and their dependence on the operating parameters of an apparatus.

The cooling of a sulfur drop can be conditionally divided into the following stages: detachment of a melt drop and its motion in an air flow, cooling of the liquid drop in water until its outer surface begins to undergo a phase transition, and solidification of the liquid phase with formation of the internal structure of the granule.

As our investigations have shown, the heat released in the process of motion of a drop in the air can be ignored since the time of its interaction with air is small and the temperature of the melt changes insignificantly. The thermogravitational convection inside the drop has a small influence on the thermal processes.

We will assume that the drop has a spherical shape, the temperature field is one-dimensional, and the initial temperature of the liquid drop is constant and equal to t_p. In this case, the dynamics of the thermal processes in the drop is described by a system of differential, unsteady heat-conduction equations. At the first stage ($0 \le \tau \le \tau_0$) the cooling process proceeds in the liquid phase. When the drop surface is cooled to the crystallization temperature t_s, the process of heat transfer in the drop is described by unsteady heat-conduction equations at varying boundary conditions. In the case of constant physical properties of the solid and liquid phases, the system of differential equations in the spherical coordinate system has the form [7]

$$a_i \left(\frac{\partial^2 t}{\partial r^2} + \frac{2}{r} \frac{\partial t}{\partial r} \right) = \frac{\partial t}{\partial \tau} . \tag{1}$$

at the initial and boundary conditions

$$\begin{aligned}
&0 \le \tau < \tau_0 : \quad r = 0 : \quad \partial t_1 / \partial r = 0 , \quad t\,(0; r) = t_p , \quad t\,(\tau; r \to \infty) = t_w , \quad -\lambda_1 \,(\partial t_1 / \partial r) = \alpha_\varphi \,(t_c - t_w) ; \\
&\tau = \tau_0 : \quad r = d/2 : \quad t_c = t_s , \quad \alpha\,(t_s - t_w) = \lambda_1 \frac{dt}{dr} + \frac{4}{3} (\pi q \rho) \left(\frac{r^3 - (x + dx)^3}{d\tau} \right) ; \\
&\tau > \tau_0 : \quad r = d/2 : \quad \alpha_\varphi \,(t_s - t_w) = \lambda_2 \frac{\partial t}{\partial r} ; \\
&\qquad\qquad r = x : \quad t = t_s , \quad \lambda_2 \frac{dt}{dr} = \lambda_1 \frac{dt}{dr} + \frac{4}{3} (\pi q \rho) \left(\frac{r^3 - (x + dx)^3}{d\tau} \right) .
\end{aligned} \tag{2}$$

The local heat-transfer coefficient was calculated from the equation obtained in [8] on the basis of experimental data of different authors:

$$\mathrm{Nu}_\varphi = 2 + \left(0.4 \mathrm{Re}^{0.5} + 0.06 \mathrm{Re}^{2/3} \right) \mathrm{Pr}^{0.4} \left(\frac{\eta_0}{\eta_w} \right)^{0.34} . \tag{3}$$

The system of differential equations (1), (2) was solved numerically by the difference method for a wide range of uniqueness conditions for the purpose of determining the dynamics of the solidified layer and the temperature field in the solid and liquid phases. As a result of our calculations, we have obtained the dependences of the solidified sulfur layer thickness on the time of its cooling and the polar angle as well as the temperature fields at different instants of time.

Investigation of the cooling regimes with the use of the physical model and the subsequent experimental investigations allowed us to separate three regimes of formation of granules depending on their structure and quality. Two main factors significantly influence the quality of the granules obtained: the rate of their cooling and the change in the heat-transfer coefficient along the perimeter of a granule. At a high rate of cooling, a sulfur melt drop solidifies with the formation of a glasslike crust on its surface. The solidification leads to a decrease in the volume of the granule formed and a decrease in the pressure inside it. Because of the small value of the heat-transfer coefficient in the middle cross section of the sphere, the solidified layer has a small thickness at this site (Fig. 1) and it is deformed in

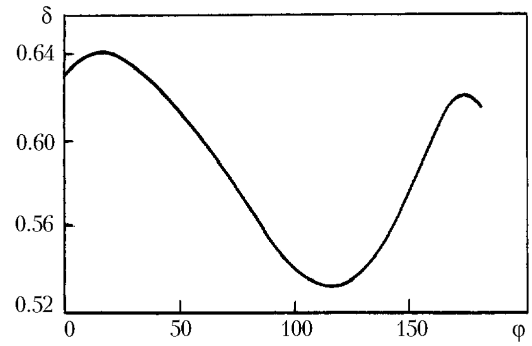

Fig. 1. Distribution of the solidification boundary at a sulfur temperature of 125^{o}C.

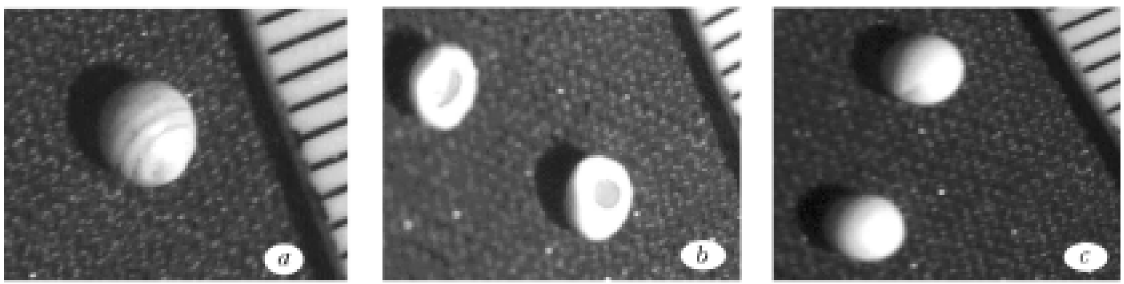

Fig. 2. Shape of sulfur granules at a high (a), low (b), and optimum (c) rate of their cooling.

the form of a ring. The solidified layer can be subjected to a repeated deformation with the result that the granule takes a step-like shape with clearly defined ring shelves at the deformation sites. A granule having such a shape is shown in Fig. 2a.

The small plasticity of the solid phase on the surface of the drop, the high rate of its cooling, and the deviation of the shape of the granule from the regular sphere lead to the accumulation of thermal stresses inside it. These changes in the shape and structure of granules are responsible for the dust arising in the process of their transportation. In such granules there arises a shrink hole connected, through a small-size capillary channel, with their outer surface. This channel is usually not seen visually. Because of the rarefaction arising in the process of solidification, the cavity is filled with water. Since the dimensions of the capillary are small, the moisture cannot be removed mechanically. Because of this, after the surface moisture is separated, the moisture content of granules obtained at high rates of cooling is higher than that of granules obtained under other conditions. Comparison of the curves of the kinetics of drying of granules obtained under various conditions shows that the above-mentioned granules are also difficult to dry.

At high temperatures of the water and sulfur, the water penetrating into the fracture on the surface of a granule comes to the boil and, in doing so, breaks down the granule. The water carrying fragments of granule shells is easily removed by a mechanical method. Sharp edges of shells formed at the sites of their fracture break down under loads. Such granules do not satisfy the standard requirements. They are shown in Fig. 2b.

Under certain temperature conditions, a slow cooling of a melt drop leads to the formation of a crust whose thickness is practically independent of the coordinate. Granules obtained under such cooling conditions have a dead (seen visually) surface. The formation of a shrink hole on a granule leads to the fracture of its surface, with the result that water penetrates into the granule shell, and, depending on the shell strength, the fracture has different dimensions. The shrink hole can further develop, and its further formation proceeds in two ways, depending on the cooling conditions. A small-size channel is formed under relatively low temperatures. The amount of penetrating water is small and its motion is made difficult by the rapid solidification of the liquid sulfur along the channel. The examination of the internal structure of granules obtained under these conditions has shown that in them there arises a solid shell of irregular shape with a capillary channel connected with the shrink hole. Such granules have a resistant surface and are

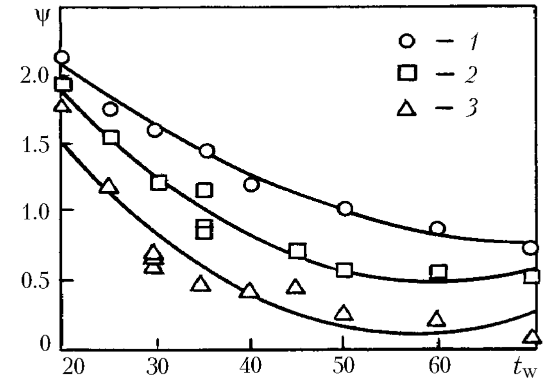

Fig. 3. Dependence of the moisture content of granules on the conditions of obtaining them: t_1 = 125 (1), 130 (2), and 135°C (3).

similar in shape to a regular sphere, and their capillary moisture content is lower as compared to that of granules obtained under other conditions. Such granules are shown in Fig. 2c.

Analysis of the heat-transfer processes inside granules has shown that their cooling can be terminated once a crust fairly resistant to preventing the fracture of the surface of granules in the process of their removal from the apparatus is formed. At this stage, the shrink hole is not yet completely formed and the internal hole is partially filled with liquid sulfur. The amount of water contained in a granule is small. The residual heat is sufficient for additional drying of the product to the moisture content satisfying the standard requirements. There is no need to equip an apparatus for granulation of sulfur, operating in this regime, with additional driers.

The efficiency of operation of an apparatus for granulation of sulfur is determined by the moisture content of the granules obtained. The moisture removed from the apparatus can be conditionally divided into the surface and capillary moisture. The surface moisture content depends on the method of removal of granules from the heat-transfer medium and the operating parameters of the apparatus. The surface moisture is easily removed by mechanical methods, such as shaking on a sizing screen, centrifuging, etc. This moisture is separated with the use of standard equipment; therefore, its removal is fairly inexpensive. The capillary moisture is removed only in the process of drying, which calls for special drying equipment and an additional expenditure of heat energy. The amount of moisture contained in granules is determined by their sizes, the site of disposition of the shrink hole, and the structure of the capillary connecting the surface with the shrink hole. The capillary moisture content depends on the heat-transfer processes occurring in granules, the size, shape, and site of disposition of the shrink hole, and the time for which the granules are found in the water.

The processing of the experimental data has shown that the moisture content of granules is substantially dependent on their sizes (Fig. 3). At a melt temperature of 125°C and a water temperature of 40°C, an increase in the average diameter of granules from 1.5 to 4 mm leads to an increase in the percentage of water in them from 0.5 to 1%. The largest increase was observed in the case where the average size of granules increased from 1.5 to 2.5 mm. This is explained by the mechanism of shrinkage of the granule material. First, the liquid sulfur moves from the center of a granule to the initial solid crust formed near the surface. Second, the sulfur solidified at temperatures close to the crystallization temperature has an insufficient strength and can be partially deformed.

Comparison of the calculated and experimental data on the rate of growth of a solidified sulfur layer shows that, if this layer has a thickness of 0.7–0.8 mm, it is in a plastic state. Therefore, in the case of solidification of small-size granules, the plastic deformation of the surface layer significantly decreases the dimensions of the internal shrink hole.

The rate of cooling of a melt drop depends on the difference between the melt temperature and the temperature of the cooling water. A surface layer formed at the initial instant of time with the use of a low-temperature water has a higher strength as compared to an analogous layer formed with the use of a high-temperature water. The plastic deformation of this layer is small and therefore the shrinkage of its internal volume is larger. It is seen from Fig. 3 that the capillary moisture content is higher at lower water temperatures and higher melt temperatures. A decrease in

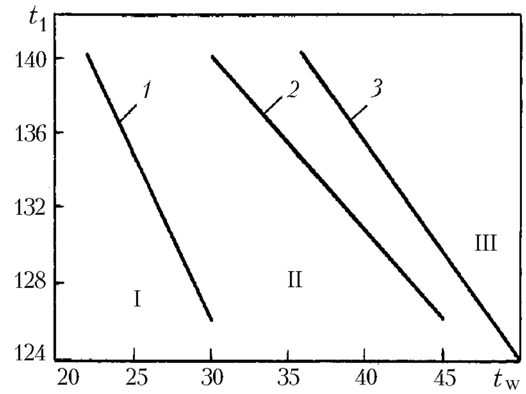

Fig. 4. Regimes of operation of an apparatus for granulation of sulfur: 1) regimes I and II for all granule sizes; 2) regimes II and III for granules with $d > 3$ mm; 3) regimes II and III for granules with 1 mm $< d \leq 3$ mm.

the rate of cooling leads to a decrease in the strength of the surface at the instant of its solidification, a decrease in the volume of the shrink hole, and an increase in the dimension of the capillary channel.

In the case of high temperatures of the melt and water, the water entering the cavity formed comes to the boil and breaks down the shell. Granules formed under such conditions are characterized by the lowest moisture content, but they do not satisfy other standard requirements.

An increase in the sulfur melt temperature decreases the capillary moisture content independently of the water temperature and the granule size; however, a decrease in the water temperature to 10–15^{o}C decreases this effect. As the investigation of the temperature fields has shown, this is explained by the decrease in the effect of the melt temperature on the temperature of the surface layer because of the high temperature head and the relatively small range of change in the melt temperature.

As was noted above, granules removed from the cooling medium can be incompletely crystallized. Such granules are characterized by a decreased moisture content, which is explained by the fact that in them there arises a shrink hole and a capillary channel free of water.

As a result of the processing of the experimental data, we have obtained a dimensionless quantity allowing for the above-indicated factors and adequately defining the regimes of operation of apparatus for granulation of sulfur by water:

$$K = \mathrm{Bi}\left(\frac{d_0}{d}\right)^{0.88}\left(\frac{1}{\theta}\right).$$

These regimes are presented in Fig. 4 and are as follows:

regime I, $K < 32$;

regime II, $32 < K < 36$;

regime III, $K > 36$.

Analysis of the experimental data obtained shows that regime II can be recommended for granulation of sulfur.

A comparison of the calculated and experimental data has made it possible to estimate the thickness of the solidified layer, the amount of liquid, and the temperature field inside a granule removed from the granulation column. The experimental data on the thickness of the water layer in the granulation column, which is sufficient to prevent the adhesion of granules to the members of the apparatus, and the calculation data on the rate of solidification of granules allow the conclusion that granules having a solidified layer of thickness 0.7–0.75 mm are sufficiently resistant to be removed from the cooling zone without fracture. The residual heat of a granule removed from the cooling medium at this stage of its crystallization gives a temperature of 70–80^{o}C.

The calculation data obtained explain the mechanism of formation of a shrink hole and its influence on the granule shape. Comparison of the experimental and calculation data shows that this phenomenon can take place in the

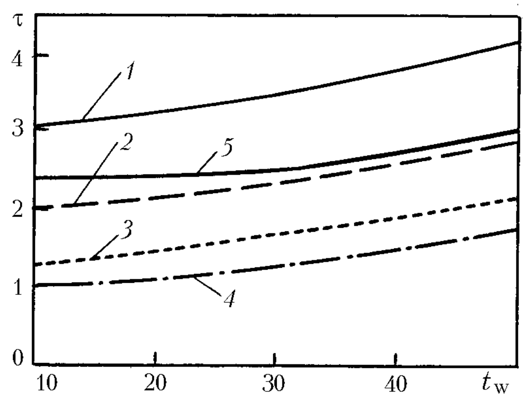

Fig. 5. Calculated and experimental dependences of the time of formation of a solid layer on the water temperature at a sulfur temperature of 135^{o}C: d = 0.8 (1), 0.7 (2), 0.6 (3), and 0.5 mm (4); 5) experiment.

case where the crust has the smallest thickness (0.4 mm) and the nonuniformity of the solidified layer thickness is more than 20%.

As the calculations have shown, the nonuniformity of the solidified layer thickness is much smaller in the case where granules are obtained in regime II. Under these conditions, a decrease in the pressure leads to fracture of the crust. Since the crust and the solidified layer have a close strength, the fracture formed has an irregular shape. Its dimensions are much larger than in the previous case because of the low strength of the surface layer, and it is rapidly filled with water.

An analysis of the experimental data on the rate of solidification of granules allows us to suggest that, at a certain thickness of the solidified layer, the surface of the sulfur melt is not deformed in the process of its motion in water. To verify this hypothesis, we compared the experimental and calculation data.

Figure 5 presents the calculated and experimental dependences of the time of formation of a resistant crust necessary for the formation of a solid layer of different thickness on the temperature of the water. Comparison of these dependences allows the following conclusions. A solid shell is not formed on the surface of a sulfur melt drop in the initial period, from 0 to 2.3–2.5 sec, of its cooling by water independently of the water temperature. The experimental line has a horizontal portion that does not coincide with the calculation data. Then the portions of the experimental and theoretical lines corresponding to the stage of further cooling go parallel to each other.

The discrepancy between the theory and experiment can be explained by the fact that the features of crystallization of melts were not taken into account in the theoretical model. Two conditions are necessary for crystallization of a melt: overcooling of the liquid and the appearance of crystal formation centers.

Analysis of the calculated temperature fields shows that the first condition is fulfilled on the surface of a drop even after 0.1–0.2 sec of its cooling. Thus, the phase transition from the liquid to the solid state is limited by the time necessary for the formation of crystallization centers. This time interval depends on the temperature conditions; however, it is difficult to quantitatively estimate it because the change in the time is comparable to the measurement error. An interval of 2.5 sec can be recommended for use in practice. It may be assumed with a sufficient degree of accuracy that the theoretical and experimental dependences will coincide beyond this interval.

The data obtained enable one to determine the necessary and sufficient time for which a sulfur melt drop should be cooled by water. Comparison of the curves in Fig. 5 allows the conclusion that, to prevent the fracture of the sulfur granule shell in an apparatus, it will suffice to hold melt drops in the cooling medium as long as the thickness of the solid layer is 0.75 mm. On this condition, the amount of moisture in the shrink hole is decreased. The crystallization heat and the heat of sulfur, released in the process of further cooling, can be used for additional drying of the product to the standard moisture content without expenditure of additional energy. Granules obtained in our experiments under such conditions had a residual temperature of 80^{o}C when they left the apparatus.

The main results of our investigations are as follows:

1. Three regimes of operation of an apparatus for granulation of sulfur by water, corresponding to different structural and qualitative characteristics of the granules obtained, have been separated.

2. The features of the cooling regimes have been investigated and the mechanism of formation of the internal structure of granules in each of them has been explained.

3. A dimensionless quantity defining the regimes of operation of an apparatus for granulation of sulfur by water has been derived and their quantitative characteristics have been determined.

The data obtained can be used for the development of apparatus for granulation of sulfur with the use of water.

NOTATION

d, diameter, m; φ, polar angle, rad, deg; ψ, moisture content, %; τ, time, sec; r, radius, m; a, thermal diffusivity, m^2/sec; λ, coefficient of thermal conductivity, $W/(m \cdot {}^oC)$; η, coefficient of dynamic viscosity, Pa·sec; δ, thickness of the solid layer, mm; α, coefficient of heat transfer on the water side, $W/(m^2 \cdot {}^oC)$; t, temperature, ^oC; x, running coordinate of the solidification boundary, m; q, melting heat, J/kg; ρ, density, kg/m^3; $\theta = (t_s - t_w)/(t_{in} - t_w)$, dimensionless temperature; Nu, Re, Pr, and Bi, Nusselt, Reynolds, Prandtl, and Biot similarity numbers, respectively; K, dimensionless quantity. Subscripts: 1, liquid phase; 2, solid phase; i = 1, 2; s, phase transition parameters; 0, minimum standard size; w, cooling water; in, initial conditions; p, initial parameters of the sulfur melt; sul, sulfur surface at the sulfur–water interface.

REFERENCES

1. D. A. Gurevich, Commercial grades of natural sulfur, special features of its storage, and transportation, in: *Problems of the Technology of Manufacture of Virgin Sulfur* [in Russian], Issue 18, Moscow (1971).
2. M. A. Menkovskii and V. T. Yavorskii, *Technology of Sulfur* [in Russian], Khimiya, Moscow (1985).
3. M. I. Zozulya, A. P. Salyuk, and R. P. Datsko, *Commercial Grades of Sulfur. Problems of Storage and Processing of Block Stock. Review: Sulfur and the Sulfur Industry* [in Russian], NIITÉKhIM, Moscow (1988).
4. P. V. Yakovlev, A. Z. Shcherbakov, and Yu. M. Biryukov, *Granulation Column*, Pat. RF 2042418, MKIZ B 01 J 2/02.
5. P. V. Yakovlev, A. Z. Shcherbakov, and Yu. M. Biryukov, *Granulator*, Pat. RF 2104765, MKIZ B 01 J 2/02.
6. P. V. Yakovlev, A. Z. Shcherbakov, and Yu. M. Biryukov, *Gravitational Separator*, Pat. RF 2100049, MKIZ B 01 J 2/02.
7. A. V. Luikov, *Heat-Conduction Theory* [in Russian], Vysshaya Shkola, Moscow (1967).
8. A. V. Luikov, *Heat Transfer: Handbook* [in Russian], Énergiya, Moscow (1978).