Agglomeration of Hematite from Aqueous Suspensions

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Synopsis

In this paper the results obtained by a laboratory scale batch test for the agglomeration of hematite from aqueous suspension are summarized. A large scale manufacture must be examined, in order to industrialize the agglomeration method. In the industrial scale process, the following points should be remarked.

The compression strength of green pellets produced by the agglomeration method with coal tar as the bridging liquid takes a minimum value at the drying temperature range of 300° to 600°C. To solve this problem, the following methods can be considered.

(1) Establishment of the drying process at the temperature range of 300° to 600°C.

(2) Agglomeration by the use of bridging liquid which is not fixed at the temperatures of 300° to 600°C. The increase of the amount of coal in pellet decreases the compression strength of reduced pellets. Therefore, the amount of coal in pellet should be kept down as low as possible in order to avoid the degradation of pellets.

I. Introduction

In general, flotation concentrates of iron ore are desired to be agglomerated before they are subjected to the smelting process. However, when the surfaces of iron ores are hydrophobic, it is very hard to agglomerate them to the green pellets of high strength. To solve this problem, the reversed flotation method seems to be effective because the iron ore surfaces are prevented to become hydrophobic. This method is made by depressing iron ores with starch or its derivatives. Iwasaki et al. have reported about the removal of fatty acid coatings from flotation concentrates.

In the current study, experiments have been made on the agglomeration method of hematite without the removal of fatty acid coatings from aqueous suspensions by the use of coal tar as the abrading liquid. The wet pelletizing method in which the separation of liquid and solid, and agglomeration of finely divided solids from aqueous suspension can be simultaneously performed, has recently become of general interest in the fields of mineral separation and water pollution disposal.

On the other hand, Yusa and Gaudin have invented the pelletizing method of finely divided solids from aqueous suspension by the use of polyacrylamide as the flocculant.

In this paper, it will be also discussed about the agglomeration of hematite pellets containing coal.

By the use of appropriate conditioning agents, as in flotation, it can be possible to condition the one desired component of a mixture and to collect this fraction as the spherical agglomeration.

This agglomeration method is advantageous for the simultaneous performance of agglomeration and mineral separation.

II. Materials

The iron ore used in the agglomeration test is hematite mined in Brazil containing 58.4% iron. Hematite was chosen as the material for the test because it was practically possible to recover hematite ore by the fatty acid flotation.

The hematite lump ores were crushed with a gyratory crushe to the powders of -10 mesh. The powders were ground with a ball mill (inside diameter-25 cm, length-30 cm, ball diameter-4 cm, revolution rate-65 rpm) for 15, 30, 60, and 120 min respectively.

Specific surface area of the grinding product was determined with the aid of a Yanaco gas chromatograph model-G8. The results obtained are shown in Table 1.

As the bridging liquid, commercial coal tar made of Tokyo Gas Co., Ltd. which is containing 0.02% ash and about 45% volatiles up to 110°C, was used. In

<table>
<thead>
<tr>
<th>Product (Grinding time)</th>
<th>Specific surface area (cm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>1070</td>
</tr>
<tr>
<td>15 min</td>
<td>2420</td>
</tr>
<tr>
<td>30 min</td>
<td>3940</td>
</tr>
<tr>
<td>60 min</td>
<td>5470</td>
</tr>
<tr>
<td>120 min</td>
<td>8720</td>
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Table 1. Specific surface area of grinding products of hematite

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order to make the surface of hematite ore hydrophobic, Na-oleate on the market was employed.

The coal mixed in the pellet was supplied by Taiheiyo Coal-Mining Co., Ltd. and was ground with a ball mill to the powder having the particle size of 40%, −400 mesh before mixing.

### III. Experimental Apparatus and Method

As shown in Fig. 1, the pelletizer consists of a horizontal outer cylinder (15 cm-diameter, 30 cm-length), and an inner one (7.5 cm-diameter, 20 cm-length).* Both cylinders can be revolved independently in variable speeds, and are made of transparent plastics so as to observe the inside.

The flotation experiment was made as follows. The hematite ore ground for 120 min were pulped to 20% solids in a FW-flotation cell having a capacity of 400 ml, and a fixed amount of Na-oleate was added to give a conditioning time of 10 min. After it was agitated for 1 min with the addition of a drop of pine oil, the flotation was started by passing air.

The procedures of agglomeration were as follows. Brazil hematite ore ground was so weighed as to give a suspension of 25% pulp density. A fixed amount of Na-oleate was added to the suspension, which was adsorbed on the surface of hematite particles for one day long with occasional agitations.

The hematite particles were filtrated and washed, then the surfaces of the particles become to have a strong hydrophobic property.

Next, the particles were repulped in the pelletizer to a fixed pulp density, and coal tar as the bridging liquid was injected into the pelletizer in three parts. During the injection, the inner cylinder was rotated to disperse the coal tar. After the injection, the inner cylinder was stopped, and the outer one was rotated for 3 min. Those operations were repeated three times. The agglomeration times was measured from the time that the outer cylinder was rotated after the addition of last part of coal tar.

After a fixed agglomeration time, the agglomerated pellets were removed from the drum and gently screened with a 10 mesh sieve, then dried at 105°C to 110°C before weighing.

For the agglomeration test of hematite pellets containing coal, the coal pretreated with a small quantity of coal tar was added to the hematite suspension in order to avoid the floating of coal powders on the air-water interface owing to their native hydrophobic property.

The strength of the pellets was measured with a pellet strength machine made of Showa Sokki Co. Ltd. The maximum of load in the force-deformation curve divided by the crosssectional area of the pellet was defined as the compression strength.

### IV. Experimental Result and Discussion

#### 1. Amount of Na-oleate Added and Hydrophobic Property of Hematite Surface

As mentioned in the introduction, the agglomeration of hematite from aqueous suspension is attainable by the use of coal tar as the bridging liquid, utilizing the hydrophobic property of hematite surface after oleic acid flotation. First of all, it is necessary to know the relation between the amount of Na-oleate added and the surface state of hematite particles.

Figure 2 shows the relationship between the flotation recovery and the amount of Na-oleate added in the case of oleic acid flotation of the powder ground for 120 min. It is found from Fig. 2 that nearly all the hematite particles float by the addition of Na-oleate of 900 g/t to 4 kg/t, but if the amount exceeds 4 kg/t the recovery falls. These facts can be considered as follows; if the amount of Na-oleate added is appropriate, the particles become hydrophobic due to the adsorption of Na-oleate on the surfaces of the hematite particles, but the addition of excess Na-oleate causes the bimolecular layer adsorption which makes the surface hydrophilic and decreases the recovery.

The effect of Na-oleate added on the agglomeration efficiency** is shown in Fig. 3. The experimental conditions adopted are as follows: the amount of coal tar added as the bridging liquid is 6 cc for 100 g hematite, the pulp density is 10% solids, the drum speed is 20 rpm, and the agglomeration time is 30 min. The hematite pellets are hardly agglomerated when Na-oleate of 500 g/t is added. In the case of 1 kg/t addition, the agglomeration efficiency increases rapidly up to 45%, but the increasing rate of efficiency becomes

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* Shell Pelletizing Separator of vertical type has been made.

** Defined in IV. 2. 1.
slow when the amount of Na-oleate added is 4 kg/t or more. Since the monolayer adsorption of oleic ions is nearly completed when 4 kg/t of Na-oleate is added, extra addition of Na-oleate more than 4 kg/t gives no influences on the hydrophobic property of the surface followed by washing. Then the agglomeration efficiency becomes nearly constant.

From these facts, it can be understood that the agglomeration efficiency becomes maximum when the hydrophobic property becomes maximum, where the oleate ions are considered to be adsorbed into the closest packed monolayer. One of the authors has reported\(^1\)\) that oleic ions are adsorbed to the bimolecular layer where further adsorption is restrained when hematite particles are treated with a large amount of Na-oleate, and that the monolayer caused by chemical adsorption is not removed by washing with water but the outer layer being adsorbed physically is easily removed by washing. This proposition is well supported by the results of the above mentioned tests of flotation and agglomeration. It means that the agglomeration efficiency becomes maximum by the formation of monolayer of the oleic ions on the hematite surfaces treated with Na-oleate of 4 kg/t. So that, in the following examinations, hematite particles treated with 4 kg/t Na-oleate are used as the sample.

2. Agglomeration Test

1. Agglomeration Efficiency

In the agglomeration test of superphosphate, Fogel\(^2\)\) has defined the yield of pellets ranging from 1 to 4 mm in diameter as the agglomeration efficiency. On the other hand, Toma\(^3\)\) has regarded the yield of pellets having the diameter of the desirable value ±2 mm as the agglomeration efficiency in the test of finely-divided coal. In this study, however, the ratio between the weight of dried agglomerates (at 105\(^\circ\) C to 110\(^\circ\) C) and the total amount of solids in suspension and added coal tar is taken as the efficiency for the sake of convenience. If the amount of coal tar is neglected, the efficiency sometimes exceeds 100\(^\%\), because the amount of coal tar remained in the pellets is more than the half even when the pellets are dried at 100\(^\circ\) C.

As the factors giving some influences on the agglomeration efficiency, the amount of coal tar, the number of drum revolutions, the drum speed, and the pulp density are enumerated. The followings are the experimental results obtained.

Figure 4 shows the relation between the agglomeration efficiency and the amount of coal tar added on the agglomeration of the hematite powders ground for 30 and 60 min. The

![Fig. 4. Relation between the agglomeration efficiency of fine grinded hematite and the amount of coal tar added](image)

Figure 5 shows the influence of the drum rotational speed on the agglomeration efficiency. The

![Fig. 5. Influence of the drum rotational speed on the agglomeration efficiency](image)
experimental conditions adopted are: Na-oleate-4 kg/ton, pulp density-10%, and drum speed-20 rpm. The efficiency increases rapidly with increasing number of drum revolutions, but it becomes nearly constant at about 300. Therefore, approximately 15 min is considered to be satisfactory agglomeration time when the drum is rotated with 20 rpm.

By changing the pulp density in the range of 5 to 30%, no influence was found on the efficiency.

2. Size Distribution of Pellets

Generally, the size of pellets is 10 to 30 mm, in diameter. In this paper, for the sake of convenience, 10 mesh (1.651 mm) agglomerates were defined as pellets as previously mentioned.

Figure 7 shows the effects of the amounts of coal tar added on the size distribution of pellets. Experimental conditions adopted are the same as those of Fig. 4. Figure 7 shows that the mean particle diameter of agglomerated pellets becomes larger with increasing amount of coal tar added. The effects of pulp density on the size distribution are shown in Fig. 8. The test was made under the following conditions; Na-oleate-4 kg/ton, coal tar added as the bridging liquid 6 cc for 100 g hematite, drum speed 20 rpm, and agglomeration time-30 min. Figure 8 indicates that the mean diameter of agglomerates decreases as the density increases. This fact suggests that the compression acting to the pellets increases as the amount of feed load in the drum increases, and the pellets are compressed or broken.

The size distribution of pellets is not affected by the number of drum revolutions. But the more the drum speed increases, the more the mean particle diameter tends to decrease. This phenomenon can be explained alike as the case of the feed load.

Therefore the mean particle diameter is controlled principally by the amount of coal tar added, and it is influenced more or less by the pulp density and the drum rotational speed.

3. Comparison of the Agglomeration in Water with the Agglomeration in Air

In this paper some considerations have been made about the agglomeration method using rotational drum. The first granules of irregular shape, so called nuclei, are formed immediately after a charge of material containing moisture is placed in the pelletizer and the drum is rotated. Then the granules are compacted by the torque of the rotary motion, and an excess moisture exude on the surfaces of the granules. This excess moisture causes cohesion of other smaller granules, and the growth of green pellets occurred.

The factors giving some influences on the growth of green pellets are the shape of material particles, size distribution, specific surface area and wettability of the material, viscosity and surface tension of the bridging liquid, as the properties of material and bridging liquid, and the amounts of binder added, rotational drum speed, number of drum revolutions, and the amounts of feed load in the drum, as the operational factors which are variable quantities.

Some explanation will be given only on the operational varying quantities:

1. Amount of binder added

Regarding to the influence of the amounts of binder added on the agglomeration efficiency, it is recognized in the results obtained by Newitt's and by ours (Fig. 7) that the diameter of pellets grows with increasing amount of binder added.

2. Rotational drum speed

Newitt and Fuerstenau have studied on the agglomeration in air and reported that the rate of granule growth, if expressed in terms of drum-revolutions, was independent of the speed, although much more time was required to produce granules of a given size at the lower speed.

In contrast with that, the mean diameter of pellets decreases with the increase of the rotational drum speed in the agglomeration in water.

3. Number of drum revolutions

The mean diameter of pellets increases with increasing number of drum revolutions in the agglomeration in air, but the number of drum revolutions has no
significant effect on the rate of granule-growth in the agglomeration in water.

(4) Drum loading

Newitt and Conway-Jones have reported that a higher loading gave an increased growth rate of closely sized fine sands. On the other hand, Fuerstenau have observed that the amount of feed load in drum had no influence on the kinetics.

In the agglomeration in water, on the contrary to the results of Newitt, the mean pellets diameter decreases with increasing feed load in drum.

From the facts described above, it may be concluded that the process such as the balling of the snow is not found in aquea pelletizing, and the granul growth completes for a short period of time, so the mechanism of aquea pelletizing is different from that of the agglomeration in air.

However, the authors must leave the detail agglomeration mechanism for a future study.

3. Strength of Pellets

Mechanical strength is cited as one of the important qualities required for green pellets. The strength consists of the drop strength which stands against the dropping and the shock of carriage from pelletizer to fired furnace, and of the compressed strength to stand against the load of pellets in the furnace. It has been found that bentonite generally used as the binder showed a remarkable effect upon the improvement of physical characteristics, including mechanical strength, of green pellets.

The relation between the specific area of row materials and the strength of green pellets is shown in Fig. 9. The tests were made under the following conditions; Na-oleate–4 kg/t, pulp density–10%, drum speed–20 rpm, amount of coal tar added–6 cc for 100 g hematite, and agglomeration time–30 min. The green pellet, if it is loaded, is not crushed but deformed. This deformation gives a crack, which is shown in the force–deformation curve as a peak. In this work, the peak of force devided by the cross-sectional area of the pellet is defined as the strength of pellet. Figure 9 shows that the strength increases with increasing specific surface area of row materials. Up to the present, there are a large number of studies on the relation between the strength of green pellets and the specific surface area or the particle diameter of row materials. For example, Newitt, Rumpf, Inoyan, and Aoki have reported on the pendular motion between the strength of green pellets and the particle diameter of row materials.

In Fig. 10, the effect of drying temperature on the compression strength of dry pellets is shown. The pellets dried at 110°C for 2 hr is further dried at a higher temperature for 1 hr. The conditions of this experiment are as follows; Na-oleate–4 kg/t, pulp density–10%, drum speed–20 rpm, agglomeration time–30 min, and the amount of coal tar added–6 cc for 100 g hematite. The compression strength, increasing with the rise of drying temperature, shows the maximum at about 250°C. Above this temperature it decreases and becomes extremely weak in the range where, \( \sigma \propto \frac{\gamma}{d} \propto \gamma S \)

Fig. 9. Relation between the specific area of raw materials and the strength of green pellets

Fig. 10. Effect of the drying temperature on the compression strength of dry pellets

Fig. 11. Relation between the compression strength of dry pellets and the amount of volatile matter of coal tar in pellets

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of 400° to 500°C. The transformation of pellets with capillary binding force to that with pendular force occurs by the volatilization of coal tar. The reason why the compression strength increases in this process, is not clarified yet. The decomposition of coal tar in pellet by firing makes the decrease of the compression strength. But the strength of pellets increases again at the temperature of 600°C or more because of the sintering of hematite particles.

The relation between the compression strength of dry pellets and the amounts of the volatile matter of coal tar in pellets is shown in Fig. 11. This figure shows that the compression strength increases with increasing grinding time, namely, the increase in the specific surface area. It is noticed that the larger the specific surface is, the sharper the peak of the curve is, and that the control of the optimum condition is difficult in this case. The compression strength shows a maximum value when coal tar contained in the pellet decreases from 9~10% to 2~3% by drying.

4. Hematite Pellets Containing Coal

The coal tar is burnt away at low temperature as mentioned above. So the coal tar does not give any contribution to the reduction of hematite. Then, the inherently hydrophobic surface property of coal was used and the agglomeration of pellets containing coal was tried.

The effect of the amount of coal tar added on the agglomeration efficiency of hematite pellets containing coal is shown in Fig. 12. The agglomeration efficiency shown in Fig. 12 is defined as 10 mesh (1.651 mm) agglomerates dried at 105° to 110°C against the total amount of solids in suspension and coal tar added. As mentioned in Section II, about 45% of coal tar volatilizes at 105° to 110°C, accordingly the agglomeration efficiency is calculated as 85% at the addition of 33 cc coal tar, if the solid and coal tar are perfectly recovered in green pellets. Practically, the existence of solids was not found and clear water was obtained after the agglomeration.

Also in this test, it is recognized that the size of pellets becomes larger and more spherical. As mentioned above, in the agglomeration of pellets containing no coal, the strength of pellets decreases when the amount of coal tar added is increased to raise the agglomeration efficiency, and it becomes difficult to recover as green pellets. In the agglomeration of pellet containing coal, as the coal takes a part to increase the amount of coal tar, the efficiency is improved and the size of pellets becomes large.

The pellets agglomerated by this method, dried at 110°C, have the strength of 7 kg/cm², although the strength of pellets prepared by using water as the binder is small because the coal does not become familiar with the water on account of its hydrophobic property.

5. Reduction Test of Pellets

The prereduced pellets have several advantages to increase the productivity and to decrease the coke ratio in blast furnace. Two methods, by the use of reducing gas, and by firing of pellets containing reducers, were used to reduce the pellets. The agglomerated pellets are suitable for the latter. On this method, there are some reports written by foreign investigators, Tate, and also by the authors.

The reduction test was made by keeping the pellets in a crucible in an electric furnace—raising temperature time (5 min), constant temperature time (15 min), cooling time (5 min).

The effect of reducing temperature on the metallization of pellets is shown in Fig. 13. The degree of metallization increases with increasing reducing temperature and seems to reach almost its limit at 1 200°C. Accordingly, the pellets in the following tests were reduced at 1 200°C.

Figure 14 shows the relation between the degree of metallization and the coal content in pellets. Though the degree of metallization of pellets containing no
coal is about 5%, that of pellets containing 30% coal raises up to 90%.

It is desirable to decrease the amount of coal in pellets as much as possible, because the addition of coal inevitably lowers the iron grade concentrated by dressing. So, the reduction of pellets containing coal together with coke has been examined.

The relation between the degree of metallization and the amounts of coke added is plotted in Fig. 15.

Figure 15 shows that the degree of metallization of the pellets is about 90% when the hematite pellets containing 20% coal are reduced with 10% coke. The degradation of pellets in the metallization process could not be recognized, and the compression strength of reduced pellets of which the degree of metallization was 90% decreased from 32 to 8 kg/cm² when coal contained in pellets increased from 10 to 20%.

V. Conclusions

(1) Finely-divided hematite, which was pretreated with a Na-oleate solution, in aqueous suspensions can be agglomerated by applying suitable agitation in the presence of a small amount of coal tar.

(2) When the surface of hematite particles is covered by the complete monomolecular film of oleate ions, the agglomeration efficiency becomes maximum.

(3) With an increase of the amount of coal tar added, the agglomeration efficiency and the pellet size increase but the strength of green pellets becomes weaker; the use of an excessive amount of coal tar results in no agglomerates formation. Thus, the amount of coal tar should be optimized.

(4) The agglomeration efficiency, determined by the amount of coal tar added to the hematite in aqueous suspensions, is not influenced by the pulp density of suspensions.

(5) The dry strength of the pellets rises up to 70 kg/cm².

(6) The agglomeration efficiency is improved and the size of pellets becomes large (more spherical) by using coal together with coal tar.

(7) When the hematite pellets containing 20% coal are reduced with 10% coke, the degree of metallization of the pellets is about 90%.

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