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COAL AND PYRITE SEPARATION
BY OIL AGGLOMERATION IN SALT SOLUTIONS

Particle suspensions of hydrophobic Upper Freeport coal from Pennsylvania
or mineral pyrite from Peru or mixtures of these materials were agglom-
erated with heptane and recovered by screening. For this process the
particles were suspended in aqueous salt solutions. Coal recovery
increased as the salt concentration was raised, whereas pyrite recovery
decreased. Consequently, the separation efficiency was improved by
increasing the salt concentration. The increase in coal recovery
appeared to be due to compression of the electrical double layer
surrounding each coal particle.

Introduction

It was known for a long time that froth flotation of hydrophobic mate-
rials such as coal could be conducted advantageously in salt solutions (1-5).
By using relatively large concentrations of ionizable salts, the consumption
of organic reagents was reduced or eliminated while at the same time increas-
ing the rate of flotation. Recently the concept of salt flotation was applied
to the beneficiation of coal fines which had first been agglomerated with a
small amount of kerosene (6). Also recently Yang et al. (7) demonstrated
several benefits of using salt solutions in the straight oil agglomeration
process for recovering and cleaning coal fines. Thus it was shown that coal
recovery with a limited amount of oil increased markedly as the salt
concentration was raised, therefore, making it possible to reduce oil
consumption. The effect of the added electrolyte appeared due to compression

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of the electrical double layer surrounding individual particles. This
explanation was also offered to account for the advantages of salt flotation
(8,9). The same explanation may apply for both processes since both are
controlled to some extent by the surface properties of the materials which are
separated and recovered.

The present work was undertaken to extend the research of Yang et al. (7),
particularly to the separation of mixtures of coal and pyrite by oil
agglomeration in salt solutions. To explore the more fundamental aspects of
the process, relatively pure materials were utilized including Upper Freeport
coal from Pennsylvania and pure mineral pyrite from Peru. These were
agglomerated separately and mixed together to determine the effect of salt
concentration while using heptane as an agglomerant. A specially designed
closed system was employed to agglomerate particles in the absence of air,
since it had been shown that entrapment of air in the agglomerates could
affect the results (10).

Materials and Experimental Methods

Two samples of Upper Freeport coal were obtained from the Lucerne No. 6
mine in Indiana County, Pennsylvania. One of these was a channel sample with
an ash content of about 27% and total sulfur content of 1.5%. The other
sample was handpicked and had an ash content of about 8% and total sulfur
content of 1.8%. Relatively pure mineral pyrite from Peru was obtained from
Ward's Natural Science Establishment, Rochester, NY. These materials were dry
ground in a high speed impact mill and then screened. The coal particles used
for most experiments had a screen size between 37 and 74 μm. and a volume mean
diameter of 47 μm. The pyrite particles had a screen size between 44 and 74
μm. The agglomerant was n-heptane from Eastman Kodak Company; its specified
boiling point of 98°C indicated a high degree of purity. Deionized water
having a resistivity of 17.9 megohm-cm. was used.

A specially designed closed system was used for the oil agglomeration
experiments to permit processing without air being present (10). The system
utilized the motor and agitator from a 14-speed kitchen blender, but the open
container furnished with the blender was replaced by a 500-ml. glass canning
jar. A small hole was drilled in the bottom of the jar. In operation the jar
was inverted, and the small hole was plugged with a rubber septum. Oil was
introduced with a hypodermic syringe through the septum. For each experiment
the jar was completely filled with an aqueous suspension containing either 10
g. coal or 3 g. pyrite or a mixture consisting of 9 g. coal and 1 g. pyrite.
The suspension was initially conditioned for 2-3 min. at high speed (about
18,000 rpm) and then a predetermined amount of heptane was introduced.

Agitation was then continued at high speed for several minutes to produce agglomerates. The agglomerates were recovered on a sieve with 149-μm. openings, dried in an oven at 100-110°C, and weighed. When mixtures of coal and pyrite were treated, the total sulfur and ash contents of the product were determined and sulfur and ash balances were used to calculate the recovery of coal and pyrite, respectively.

Results and Discussion

In order to determine the effect of mixing time on coal or pyrite recovery when the particles were suspended in a salt solution, a series of experiments was conducted in which the time of mixing was varied after adding heptane. The results presented in Figure 1 were obtained by treating separately Upper Freeport coal or pyrite in the closed system. For these experiments Upper Freeport coal was employed which had an ash content of about 8% and a mean particle diameter of 47 μm. It can be seen that a relatively high recovery of coal (70-80%) was realized over a wide range of mixing times with 5 v/w % heptane (i.e., 0.5 ml. heptane/10 g. coal) when the coal was suspended in 1.5 M sodium chloride. Moreover, coal recovery was not affected significantly by mixing time over the range of 1 to 5 min. The recovery of pyrite was much lower than that of coal even though the relative oil dosage (33 v/w %) was much greater. Also the recovery of pyrite was more sensitive to mixing time than the recovery of coal. The maximum recovery of pyrite occurred after 3
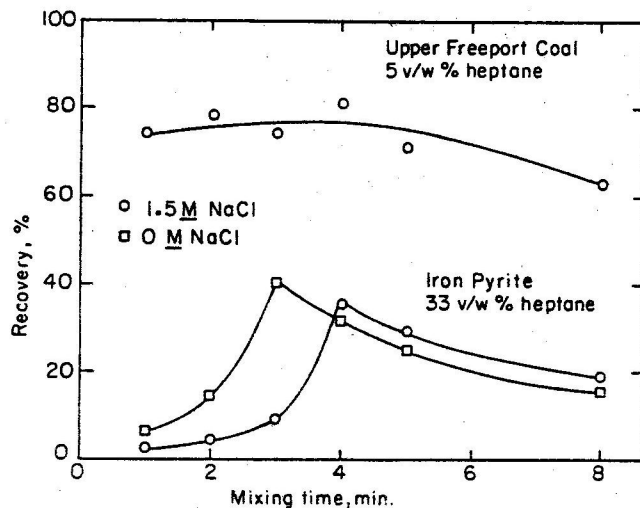

Fig. 1. Results of agglomerating 10 g. coal or 3 g. pyrite in the closed system.
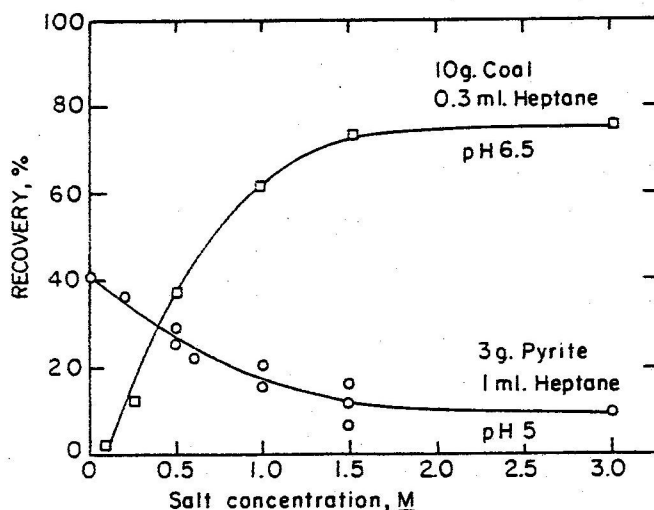
Fig. 2. Results of agglomerating coal or pyrite separately in the closed
        system, after mixing for 2 or 3 minutes.

min. of agitation in a water suspension or after 4 min. of agitation in a salt
solution.

    To see how salt concentration affected the agglomeration recovery of Upper
Freeport coal or pyrite, a set of agglomeration experiments was conducted in
which the salt concentration was varied while other conditions were held
constant. For this set of experiments a portion of the channel sample of coal
was selected which had an ash content of 18.6%. The coal and pyrite were
treated separately with different amounts of heptane because proportionately
more heptane was required to recover pyrite than coal. After introducing
heptane, the coal suspension was agitated for 2 min. and the pyrite suspension
for 3 min. to achieve agglomeration. The results presented in Figure 2 show
that coal recovery and pyrite recovery were affected quite differently.
Whereas coal recovery increased as the salt concentration was raised, pyrite
recovery decreased. The behavior of Upper Freeport coal was similar to that
of a hydrophobic coal from New Zealand with a very low ash content which had
been treated previously (7). For coal the effect of salt concentration seemed
due to compression of the electrical double layer surrounding individual
particles. For pyrite the effect of salt concentration seemed due to the
adsorption of hydrated sodium ions on the surface of the particles which made
the particles more hydrophilic and less oleophilic. Earlier measurements by
Gaudin and Charles (11) showed that sodium ions are adsorbed significantly by
pyrite, with the quantity adsorbed being proportional to the concentration in
solution.

To analyze the effect of salt concentration on coal recovery, the recovery was plotted against the Debye-Hückel parameter κ which is proportional to the ionic strength of the solution and is given by the expression,

$$\kappa(nm^{-1}) = 2.33 \; [\sum_i z_i^2 \; \underline{M}_i]^{1/2}$$

where $\underline{M}_i$ = molar concentration of ionic species i
and z_i = valence of ionic species i.

The preceding expression applies to aqueous solutions of electrolytes at 25°C (12). The quantity in brackets represents the ionic strength and is summed over all ionic species in solution. Because κ controls the range over which the electrical forces surrounding each particle in a suspension exert an effect, κ^{-1} is commonly regarded as representing the "thickness" of the double layer surrounding each particle.

Figure 3 shows that coal recovery was directly proportional to κ over the range from 1 to 4 nm.$^{-1}$ which indicates that the recovery was inversely proportional to the "thickness" of the double layer over this range. In other words, as the double layer was compressed, the recovery increased. However, for values of κ greater than 4 nm.$^{-1}$, the recovery remained constant and apparently was limited by some other parameter such as the quantity of heptane. Other experiments which utilized different salts such as sodium sulfate or calcium chloride achieved approximately the same results as those
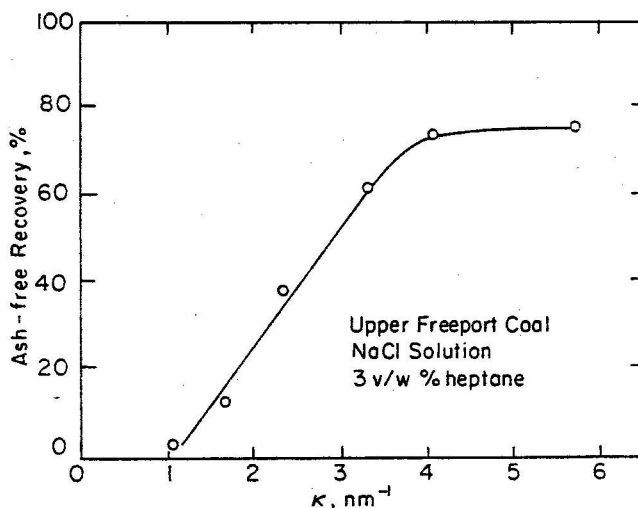

Fig. 3. Results of agglomerating coal suspended in salt solutions of increasing ionic strength.
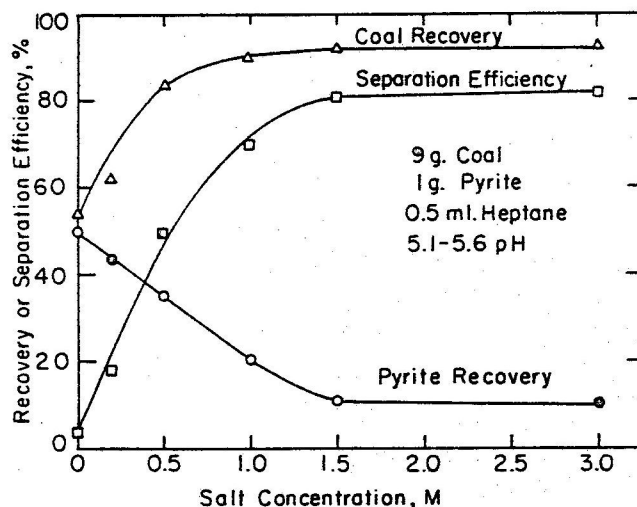
Fig. 4. Results of agglomerating a mixture of coal and pyrite.

in Figure 3. Thus different salts produced much the same effect when compared
at the same ionic strength.

To study the effect of salt concentration on the separation of coal and
pyrite, mixtures of coal with 8.2% ash and mineral pyrite were suspended in
salt solutions of various concentrations and agitated for 3 min. after adding
heptane to agglomerate the particles. The results presented in Figure 4 show
that for a salt concentration of zero, coal recovery from the mixture was 54%
and pyrite recovery 50%, resulting in a separation efficiency of only 4% as
defined below:

Sepn. Efficiency (%) = Coal Recov. (%) - Pyrite Recov. (%)

But as the salt concentration was raised, coal recovery increased and pyrite
recovery decreased resulting in a greater separation efficiency. Thus, for a
salt concentration of 1.5 M, coal recovery was 92% and pyrite recovery 11%
providing a separation efficiency of 81%. A salt concentration greater than
1.5 M achieved little additional benefit. Interestingly, the results achieved
with the mixtures corresponded rather well to the results obtained by
subjecting coal or pyrite separately to agglomeration.

Another indication of the effect of an electrolyte on the agglomeration
process was observed by comparing the bulk volume of agglomerates produced in
a salt solution with that of agglomerates produced in water. A technique
employed by Drzymala et al. (10) was used to measure the bulk volume of the
agglomerates. Upper Freeport coal with an ash content of 27% was vet ball-

milled only long enough to pass a 125 μm. screen so that it had a volume mean particle diameter of 90 μm. The wet coal was further treated with ultrasonic energy to insure complete removal of trapped air. The deaerated coal was conditioned for 2 min. in the closed agglomeration system, and after adding a measured volume of heptane, mixing was continued for 2 min. The suspension of agglomerates was transferred to a graduated cylinder and allowed to settle for 20 hr., whereupon the bulk volume of the settle material was measured. The
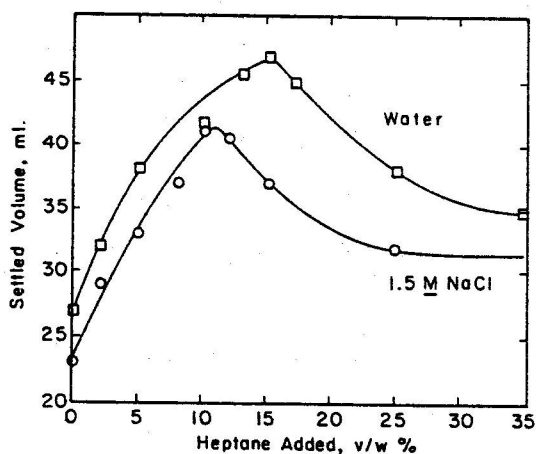

Fig. 5.   Settled bulk volume of agglomerates produced in pure aqueous or saline suspensions.

results in Figure 5 indicate that the bulk volume was affected by both the salt content of the suspension and the quantity of heptane. As the quantity of heptane was increased, the bulk volume rose, peaked, and then decreased. It has been reported that the peak in this type of curve corresponds to the transition from the pendular state of agglomeration to the funicular state (13). In the pendular state only enough oil is present to stick particles together at points of contact between particles, whereas in the funicular state more of the interstitial space between particles is filled with oil. Thus it appeared to require less heptane to reach the transition between agglomeration states when the coal was suspended in 1.5 M sodium chloride than when it was suspended in water. Also with any given quantity of heptane, the bulk volume of the agglomerates produced in a salt solution was appreciably smaller than the bulk volume of agglomerates produced in water. Hence, the agglomerates produced in salt water must have been more compact than those produced in water which apparently resulted from compression of the electrical double layer.

Conclusions

The separation efficiency of the oil agglomeration process was improved by suspending fine particle mixtures of hydrophobic Upper Freeport coal and mineral pyrite in a salt solution. As the salt concentration was raised, coal recovery increased and pyrite recovery decreased. These trends were observed with suspensions containing only coal or pyrite as well as with suspensions containing both coal and pyrite. For coal the effect of salt concentration appeared due to compression of the electrical double layer surrounding individual particles. However, for pyrite the effect of salt concentration seemed due more likely to adsorption of hydrated sodium ions on the surface of the pyrite.

Acknowledgement

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STRESZCZENIE

Chen-Wen Fan, Markuszewski R., Wheelock T.D., 1987. Separacja węgla od
   pirytu w procesie aglomeracji olejowej w roztworach soli. Fizyko-
   chemiczne Problemy Mineralurgii 19; 17-26.

Zawiesiny ziarn hydrofobowego węgla Upper Freeport (Pennsylvenia),
minerału pirytu z Peru, oraz mieszanin tych materiałów były aglomerowa-
ne heptanem i następnie odzyskane na sitach. Proces aglomeracji olejowej
prowadzono w wodnych roztworach soli. Odzysk węgla wzrastał ze wzrostem
stężenie soli, podczas gdy odzysk pirytu obniżał się, co oznacza, że
efektywność rozdziału wzrastała ze stężeniem soli. Nasze badania wska-
zują, że wzrost odzysku węgla jest wynikiem kompresji elektrycznej
warstwy wokół ziarn węgla.

СОДЕРЖАНИЕ

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   вопросы обогащения, 19; 17-26.

Суспензии зерен гидрофобного угля Аппер Фрипорт /Пенсильвания/,
минерала пирита из Перу, а также смеси этих минералов были агломериро-

ваны гептаном, а потом извлечены на ситах. Процесс маслянной агломерации проведен в водных растворах соли. Извлечение угля увеличивалось с повышением концентрации соли, а извлечение пирита снижалось, что обозначает, что эффективность раздела повышалась с концентрацией соли. Эти исследования указывают, что увеличение извлечения угля является результатом компрессии электрического двойного слоя вокруг зерен угля.