Regeneration of Spent Limonite using Gasoline. II. Continuous Countercurrent Process

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Earlier, a process of regeneration of limonite using hot gasoline on fixed bed was worked out. This study indicated the possibility of developing a countercurrent process where both gasoline and limonite could move physically in opposite directions. For this purpose, free movement of different limonite particles under gravity in still and flowing gasoline was studied. After careful consideration, regeneration column was designed for further experiments and operated under varied conditions. Optimum liquid velocity and solid-liquid contact period at different limonite velocity were ascertain and discussed. Finally, a modified process flow sheet has been drawn up and presented.

Regeneration of Spent Limonite Continuous Countercurrent Process

In view of earlier observations[1] and data obtained thereof, attempt was made to realize a continuous countercurrent process in which both gasoline and limonite could move physically. The Dorr multideck classifier was the only suitable equipment for this type of closed circuit leaching. But the fact that limonite did not get wet in gasoline and its movement was considerably free, led to think otherwise. It was thought that gravity flow of limonite through gasoline might be feasible. To achieve this end, it was first necessary to study counter-

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1) M. I. ALi, This Bulletin, 35, 888 (1962).

TABLE I. FALLING VELOCITY OF LIMONITE PARTICLES THROUGH GASOLINE UNDER GRAVITY

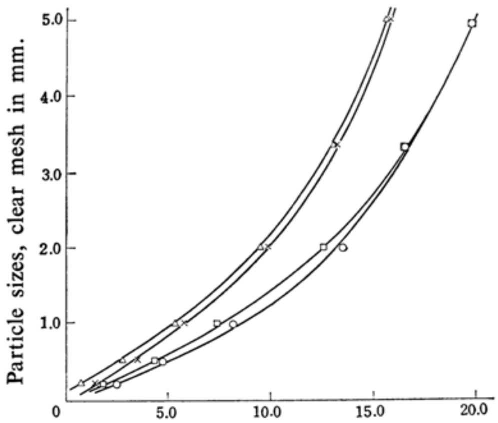
Specific gravity of gasoline;	0.84 at 16°C
Viscosity of gasoline;	1.13°E at 20°C
Height of the place of experiment above sea level;	200 m. (approx.)
Temperature during experiment;	20°C
Travelling distance of limonite particles;	2.5 m.

Particle size mm.	% of different size particles			Falling velocity of limonite particles in gasoline, cm./sec.								
	Fresh limonite	Spent limonite	Regenerated limonite	Fresh limonite	Spent limonite				Regenerated limonite			
				1	1	2	3	4	1	2	3	4
>5	23.6	3.9	5.1	23.6	23.6	—	—	—	19.7	—	—	—
3.36~5	9.8	10.4	5.7	19.7	19.7	19.7	19.7	19.7	15.7	15.7	15.6	15.6
2~3.36	12.7	26.8	14.5	15.7	16.4	16.4	16.4	16.4	13.1	13.0	13.0	12.9
1~2	14.1	24.5	22.7	9.8	13.4	12.9	12.6	12.5	9.8	9.8	9.7	9.5
0.5~1	11.9	11.7	12.7	6.95	8.1	7.8	7.5	7.3	5.9	5.8	5.5	5.3
0.21~0.5	15.0	11.0	14.8	4.23	4.7	4.8	4.6	4.3	3.6	3.4	3.1	2.8
<0.21	11.5	10.2	23.8	2.62	2.45	2.1	1.8	1.2	1.5	1.0	0.8	0.5
Fine particles	—	—	—	0.98	0.4	0.2	0.1	Stationary	<0.1	Stationary	Stationary	−0.1

Remarks:
i) 1, 2, 3 and 4 in this table correspond to the experiments with still gasoline and flowing gasoline of rates 4.9, 9.8 and19.7 ml./cm² min. respectively.
ii) For this short distance movement acceleration of the particles is neglected.
iii) Higher per cent of 5 mm. particles of fresh limonite was due to agglomerated lumps.

current flow of limonite particles through gasoline. The experiments were carried out with different size particles of fresh, spent and regenerated limonite.

Procedure. A long glass tube (2.7 m.× 160 mm.ϕ) was erected vertically. Lower end was closed and gasoline poured into it. In still gasoline the particles of limonite were allowed to fall under gravity. Time taken by individual particle to travel a distance of 2.5 m. was noted. The velocity of the falling particle was then calculated. Next, gasoline was forced to flow upward in the column at a certain velocity and the above experiments were repeated with only regenerated and spent limonite. These results are presented in Table I and Fig. 1.



Falling velocity of limonite particles, cm./sec.

Fig. 1 Change of falling velocity of Limonite in gasoline with particle sizes.
Regenerated limonite particles: in still gasoline (×); in flowing gasoline, 19 ml./cm² min. (△).
Spent limonite particles: in still gasoline (○); in flowing gasoline, 19 ml./cm² min. (□).

From the above table and Fig. 1, it appears that the average particles of both spent and regenerated limonite are not affected much by upstream flow of gasoline even at flow rate 19.7 ml./cm² min. Only the fine particles 0.5~1.0% of the mass were affected and some showing negative velocity i. e. the particles were moving upwards with flowing gasoline. If above mentioned gasoline velocity is considered as limiting velocity, then the contemplated regeneration column may be examined by the following way (Fig. 2).

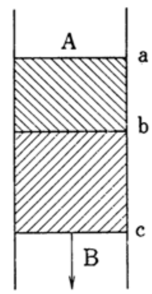


Fig. 2. Upper section of regeneration column.

Let AB is a section of contemplated regeneration column. Rich gasoline leave the column at 'a', limonite particles enter into the column at 'b' while limonite bed starts from 'c' to downwards. Then, ac is liquid zone. If only particle sizes below 0.21 mm. are considered it will be seen that 10.2% in spent limonite and 23.8% in regenerated limonite constitute this fraction. Their spatial distribution in the column may be as follows:

The spent limonite particles would normally be in zone 'bc' and below. These particles from 'b' will, of course, have slow fall and ultimately come down to c-line. At this position there should be some eddy zone e, in Fig. 3, where there is no upward movement of

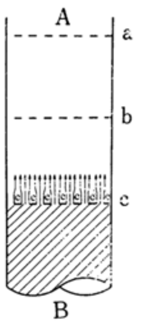


Fig. 3. Upper section of regeneration column. Arrow heads indicate gasoline flow while 'e' indicates 'eddy zones'. Other notations are same as in Fig. 2.

gasoline (rather downward) and even the stationary particles will settle on the limonite bed there. Once it is settled, it will be soon covered by the larger particles which are continuously falling on the bed. Thus covered small particles will have restricted movement and it will move down with other particles. Further, downward movement of fine particles in zone 'bc' will be enhanced by the impact of falling particles.

As regards regenerated limonite, particles below 0.21 mm. is much higher than that of spent limonite. It is due to breakage of particles during processing, and sulfur elimination. These particles are mostly at the bottom of limonite bed where its movement is much restricted. There is a little chance of its being carried by gasoline. However, a filter must be used at 'a' to take care of carried particles, if any.

In view of the above observations, it was deemed fit to realize a continuous counter current process in which both limonite and gasoline would move physically in opposite direction. Finally, a small apparatus was used to regenerate about 10.0 kg. spent limonite per

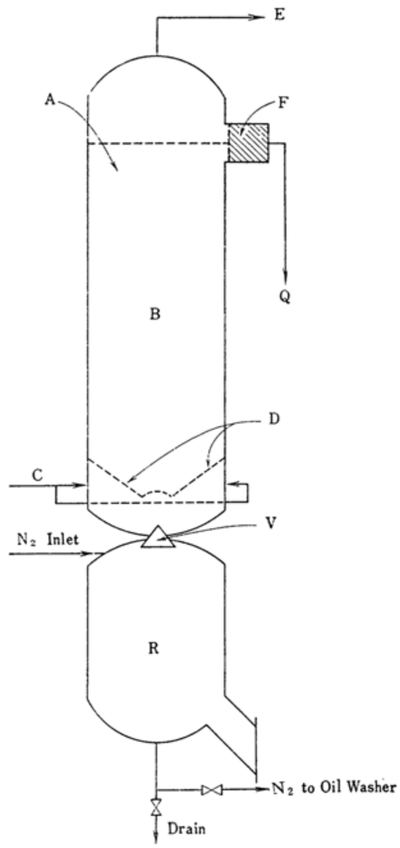


Fig. 4. Regeneration column for counter current process.
A Spent limonite inlet
B Regeneration column
C Gasoline inlet
D Distributor
E Condenser
F Filter
Q Quenching column
R Receiver (Sulfur)
V Cone valve

day. The operation was manual. In this case, other set up remained unchanged as in "hot gasoline flow process" except the regeneration column which was modified. Feeding system was changed. The regeneration column is shown in Fig. 4.

Description of the Equipments and Operation. Spent limonite was introduced into regeneration column B at A, and hot gasoline at C, under the distributor D. Rich gasoline was led to the quenching column through filter F. On opening the cone-valve V. limonite was allowed to fall down slowly to the receiver R, after regeneration. The movement of limonite was regulated by the cone-valve. Valve V was closed when the receiver was almost full. Gasoline was drained out from the receiver and nitrogen was passed for drying the mass.

After drying, the regenerated material was removed from the bottom. During drying of limonite, leaching was stopped. But it could be made continuous by installing one more receiver. The distillate gasoline was passed to the condenser E.

Equipment Specifications.—

Material movement:

a) Limonite particles; 25.0 g./min.

b) Gasoline; 360.0 ml./min.

(gasoline/limonite = 12.0)

A regeneration column (120 cm. × 10 cm. ϕ) was selected. This could operate under conditions of 0.44 cm. limonite velocity with 273 min. contact period and 7.4 cm. gasoline velocity with 16.2 min. contact period. The velocity and contact period of both limonite and gasoline is changeable. The experiments were carried out under varied conditions.

A review of contact periods of limonite in different experiments done earlier could not give any clear indication for its requirement. Therefore, special attention was paid to "contact period of limonite" in subsequent experiments. These results are presented in Table II and Fig. 5.

The above results indicate that contact period of limonite has some bearing on the recovery of sulfur at the final stage. To ascertain the behavior at earlier stages a few experiments were carried out with lower gasoline/limonite ratio. These results are presented in Table III.

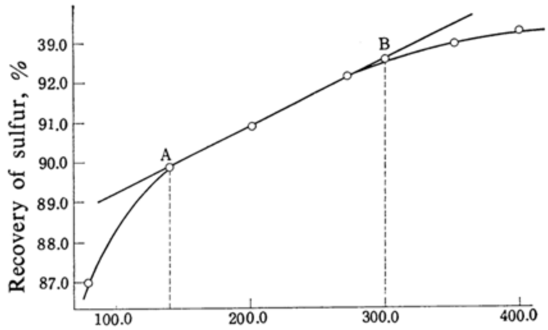


Fig. 5 Progress of sulfur recovery with contact period of limonite.

From the results in Table III it appears that at the initial stage contact period of limonite has practically no influence on sulfur recovery. As gasoline/limonite ratio increases, the effect of contact period of limonite becomes significant. This may be explained from the fact

Table II. Progress of sulfur recovery with contact period of limonite

Gasoline/limonite: 12.0; temperature: 85.0°C

Limonite Velocity cm./min.	Limonite Contact period min.	Gasoline Velocity cm./min.	Gasoline Contact period min.	Sulfur recovery %	Remark
* 1.5	80	24.8	4.85	87.0	"Overflow" and "distillate" gasoline are about 95.0% and 5.0% respectively.
0.86	140	14.2	8.45	89.9	
0.60	200	10.0	12.0	90.9	
0.44	273	7.4	16.2	92.2	
0.40	300	6.65	18.0	92.6	
0.34	352	5.7	21.0	93.0	
0.30	400	5.0	24.0	93.3	

* In this experiment some limonite particles were found to be carried over by gasoline.

Table III. Effect of contact period of limonite at lower gasoline/limonite ratio

Temperature; 85.0°C

Gasoline/limonite ratio	Limonite Velocity cm./min.	Limonite Contact period min.	Gasoline Volocity. cm./min.	Gasoline Contact period min.	Sulfur recovery %	Remark
3.0	0.86	140	3.60	33.4	49.8	The change of limonite velocity and contact period was effected by regulating the cone valve. Gasoline flow was adjusted according to limonite velocity.
3.0	0.40	300	1.68	71.7	50.4	
6.0	0.86	140	7.20	16.7	68.4	
6.0	0.40	300	3.35	35.7	69.5	
9.0	0.86	140	10.80	11.2	86.5	
9.0	0.40	300	5.00	24.0	88.8	

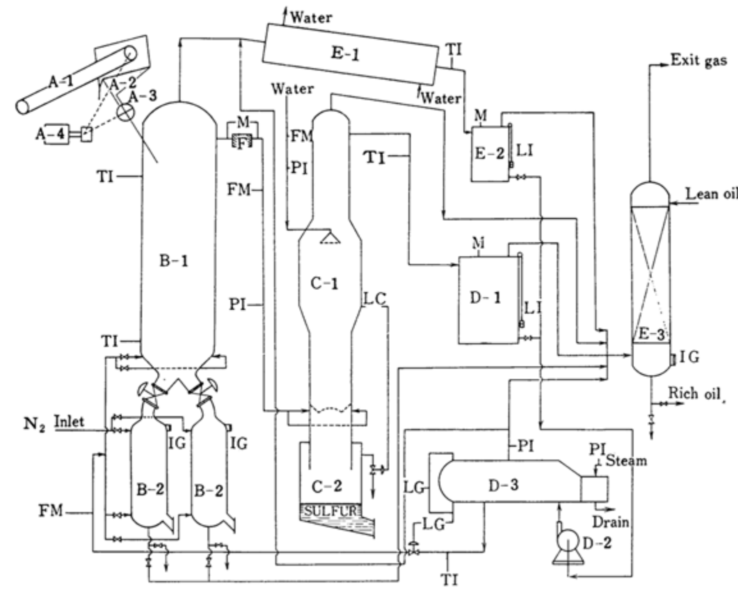


Fig. 6. Equipment flow sheet of limonite regeneration plant with control instrument.

Control instruments

Symbols and Instruments	No. regd.	Symbols and Instruments	No. regd.
FM Flow meter	3	IG Inspection glass	2
LC Level controller	2	TI Temperature indicator	5
LG Level glass	2	PI Pressure indicator	4
LI Level indicator	2	M Manometer	3

Equipments

A-1	Belt conveyor	D-1	Gasoline storage tank
A-2	Screen	D-2	Gasoline feed pump
A-3	Rotary valve	D-3	Gasoline reboiler
A-4	Motor for BC and RV	E-1	LF gasoline condenser
B-1	Regeneration column	E-2	LF gasoline storage tank
B-2	Drying vessels	E-3	Off gas scrubber
C-1	Quenching column	F-1	Filter
C-2	Sulfur settling tank		

that sulfur remains entrapped in the particles and does not come in contact with gasoline readily. It takes time. It can be explained easily from the peculiar phenomenon "the migration of iron oxide" during reverse oxidation process[2]. The liberated sulfur does not form film on the surface of the particles. On the contrary, ferric oxide migrates so that sulfur forms the core of each particle. Moreover, caking also occurs frequently due to careless operation at elevated temperature.

The effect of contact period of limonite was found to be uniform and linear between the range of 140~300 min. (AB in Fig 5). Beyond 300 min., the effect of contact period becomes insignificant. But in case of lower contact period yield was found to be low which may be due to insufficient contact period of gasoline (minimum contact period desired 6 min. for saturation (1)).

It is evident that longer contact period is desired for better efficiency. It is possible to regulate the contact period to some extent by controlling the production. It would have been much appreciating if arrangement could be made to pass gasoline through regenerated limonite using a by-pass line for final washing out of sulfur. However, a modified flow sheet for this process is presented in Fig. 6.

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2) H. B. Avery, *Chem. & Ind.*, 17, 171 (1939).