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Reclaim of Synthetic Rutile Fines Produced In Ilmenite Beneficiation Process by Agglomeration

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ABSTRACT
The synthetic rutile is used as feed stock material for producing rutile TiO_2 under chloride route method. The synthetic rutile suitable for chlorination process under fluidized bed reactor was having a specification of TiO_2 content above 90 %, silica content less than 2 %, and particle above 100 micron in size. One of the steps in the up-gradation process of ilmenite was leaching with mineral acids. The leach liquor obtained after leaching process is called spent acid. During leaching process, aberration leads to produce ultra fine particles of synthetic rutile which is found suspended in spent acid. A few amount of TiO_2 was digested in acid to form hydrated TiO_2. The spent acid contains both these ultra fine particles and hydrated TiO_2 particles which were allowed to settled and removed from the system as TiO_2 sludge. In addition to TiO_2 sludge, a small quantity (0.5 - 0.7 %) of synthetic rutile having particle size less than 100 micron (required specification) were also generated, which is removed by using cyclone and stored as synthetic rutile fines. The quantity of synthetic rutile fines and TiO_2 sludge produced are 1.0 MT and 3.0 MT respectively in a production plant having the synthetic rutile production capacity of 140 MT/day. The present invention aims to recover and re-use the synthetic rutile fines and TiO_2 sludge generated in the ilmenite beneficiation plant by agglomeration technique.

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Introduction

Titanium dioxide, a white pigment finds wide application in paint, plastic, catalytic, ink, textiles, ceramic etc., due to its excellent pigmentary properties [1-4]. The band gap of TiO_2 pigment is ranging from 3.0 - 3.2 eV, which makes its wide application in the field of photocatalysis [5-7]. Anatase, rutile and brookite are the three different crystalline forms of TiO_2 among which the rutile is the most stable form [8]. Commercial production of titanium dioxide is either by sulphate or chloride process with small extent of other processes like solvent extraction, electrochemical process etc [9-11]. The chloride process produces rutile titanium dioxide and sulphate process technology used for producing both anatase and rutile titanium dioxide. The pigmentary property of rutile titanium dioxide is superior compared to anatase, but for photo-catalysis the anatase is superior due to its large band gap of 3.2 eV [6]. For pigmentary properties, the rutile pigment produced by chloride route is superior compared to rutile pigment produced by sulphate process. In the world scenario, more than 60 % of titanium dioxide production is through chloride route. The chloride route uses ilmenite, titanium slag, synthetic rutile, natural rutile as feedstock material. Synthetic rutile is the most preferred material compared to other feedstock materials due to its high TiO_2 content (92-95 %), less other impurities like iron oxide (2-3 %), silica (0.5-1.5 %,) alumina (0.5-1.0 %) etc. There are many technologies used to upgrade the TiO_2 values in ilmenite, but the commercial production still relay on either Becher process or Benalite process. In both processes, the ilmenite is subjected to carbothermic reduction followed by leaching to reduce the iron values and upgrade the ilmenite to synthetic rutile [12].

The synthetic rutile is used as the feed stock for chlorination process for producing titanium tetrachloride. The titanium tetra chloride on subjected to oxidation with oxygen at high temperature to produce rutile titanium dioxide pigment. The chlorination process is carried out in a fluidized bed reactor and the particle size of the feed stock material is very critical in fluidization process. The draft velocity inside the chlorinator leads to the carryover of the ultra fine particles (below 100 micron) and hence these ultra fine particles will not get enough residence time for getting chlorinated. The ultra fine synthetic rutile particle does not produce titanium tetra chloride and it is removed from the chlorination unit in cyclonic separation system as dust particles. These fines enhances the generation of Effluent Treatment Plant (ETP) solid in titanium dioxide plant.

The Q-grade ilmenite (Quilon grade) which is one of the best quality of ilmenite available contains nearly 60 % of TiO_2. The fine fraction (< 100 micron) in this ilmenite is about 5 %. This ilmenite contain 25 % of ferric oxide and 10 % of ferrous oxide and balance with other impurities like silica, alumina etc. The Q grade ilmenite is available in the costal areas of Kollam district in Kerala, India.

The ferric content in the ilmenite is reduced to ferrous during carbothermic reduction at 1000 ^oC. The reduced ilmenite was subjected to hydrochloric acid leaching to remove the 90 % of iron content in reduced ilmenite. The reduced ilmenite after removal of 90 % of iron content is called leached ilmenite. The leached ilmenite is then heated at 600 ^oC in a rotary kiln to convert it to synthetic rutile which contain about 92-95 % of TiO_2. In addition of the existing 5 % fines (less than 105 micron size particle) in ilmenite, the above process of carbothermic reduction and leaching also generate fines content in the synthetic rutile. A fraction of the fines generated will carryover along with the spent acid (leach liquor), where us the balance fraction of fines are removed from the synthetic rutile after

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calcination, through cyclone system. The fines carried-over with the spent acid were settled in storage tanks by giving settling time. The fines free spent acid was feed to acid regeneration plant to regenerate to hydrochloric acid from the spent acid and again used for leaching process. The settled fines are removed as sludge which is neutralized and stored along with ETP solid. The fines fraction removed from cyclone is also is dumped along with ETP. Almost 1.0 MT of cyclone separated fines and 3.0 MT of TiO_2 sludge are generated in 140 MT /day synthetic rutile production. Presently the 4.0 MT of these fines are losing per day. Moreover, these fines increases the volume of ETP solid generated. The present invention is related to development of a selective self sintering (agglomeration) technology for size improvement of synthetic rutile fines to usable range in fluidized bed reactor producing titanium tetrachloride. Moreover, by implementing this technology, the Ilmenite Beneficiation plant will become a zero effluent discharge system.

Experimental

Materials

The typical composition of Q-grade ilmenite is given in Table 1. The TiO_2 content in the Q-grade ilmenite is 60 %, which make its superiority over other ilmenite. The high ferric content compared to ferrous showed that this type of ilmenite was highly weathered ilmenite (more aerial oxidation). The alteration of ilmenite was occurred during weathering process there by crystallography changes to pseudo brookite, pseudo rutile, rutile etc. The Typical particle size of the Q grade ilmenite is given Table 2.

Table1: Typical composition of Q grade ilmenite

Sl. No	Constituents	Percentage
1	TiO_2	60
2	$Fe2O_3$	25
3	FeO	10
4	SiO_2	1.5
5	Al_2O3	1.0
6	V_2O_5	0.12
7	Cr_2O_3	0.12
8	ZrO_2	0.30
5	Nb_2O_5	0.20

Table 2: Typical particle size of Q grade ilmenite

ASTM Mesh	Size in Micron	Percentage
+30	> 600	3
-30 +60	600- 250	32
-60+ 100	250-150	35
-100+140	150-105	25
-140	< 105	5

The fine fraction in ilmenite (less than 105 micron in size) is 5 %. These fines will loss in the up gradation process either as TiO_2 sludge or as synthetic rutile fines through cyclone.

Carbo-thermic reduction

The ilmenite was subject to carbo-thermic reduction using petroleum coke as reductant. The dimension of the kiln was 30 meter length and 2 meter diameter. The temperature inside the kiln will be around 1000 °C. The ilmenite to petroleum coke feed ratio to the kiln is 10:1. The kiln rotates at a speed of 1 rpm and thereby providing a residence time of 1.5 hour for the ilmenite reduction reaction. In reduced ilmenite, 90 % of ferric ions are converted to ferrous ions. There will be no changes in TiO_2 values in reduced ilmenite. As Fe_2O_3 is converted to FeO, there will be a slightly weight loss occurred in quantity of ilmenite.

Leaching process

The leaching process of reduced ilmenite is carried out by using hydrochloric acid in a closed digester system. The leaching process is a pressurised one with a reaction temperature of around 142 °C and pressure 3.5 kg/cm^2. The pressure was created by charging steam in to the system continously. The hydrochloric acid after leaching process is called spent acid, which will again convert to hydrochloric acid in acid regeneration plant and hence re-used. The leached ilmenite contains about 90-95 % of TiO_2 values. The fines already in the ilmenite as well as the fines generated in the beneficiation process were removed from the system either through spent acid or in cyclone discharge after calcinations. The spent acid is stored in huge tanks called settling tanks where sufficient time is given for settling of fines in spent acid before its reprocessing in acid regeneration plant. The settled fines is removed from the storage tanks as sludge which is neutralized and then stored in ETP sludge pond.

Characterization studies

The particle size distribution of the raw materials were measured by using Microtrac particle size analyzer. The crystallographic nature of the material was determined by taking XRD spectra using Rigaku XRD instrument. The zeta potential was measured by using Malven Zetasizer Z590 instrument.

Results and Discussion

Characterization of Materials

The synthetic rutile fines having aTiO_2 value of 92.5% and TiO_2 sludge was having a TiO_2 content of 93.6%. Both the TiO_2 sludge and synthetic rutile fines were having particle size < 100 micron in size. The TiO_2 sludge also contains small amount of titanium oxy chloride, hydrated TiO_2 etc., produced by the leaching reaction of ilmenite with hydrochloric acid. Figure 1 showed the photographs of decanted TiO_2 sludge and synthetic rutile fines.

Figure 1: (a) Synthetic rutile fines (b) TiO_2 sludge

Figure 1: Photographs of decanted TiO_2 sludge and synthetic rutile fines

Particle size distribution

The particle size distribution of synthetic rutile fines and TiO_2 sludge were shown in Figure 2.0. A wide distribution of particle was noticed in both cases. The particle sizes of both materials were ranged from 0.5 micron to 100 micron in size. The average particle size of synthetic rutile fines was 8.746 micron and TiO_2 sludge was 2.946 micron. Both synthetic rutile fines and TiO_2 sludge were having particle size less than 100 micron and hence cannot be directly

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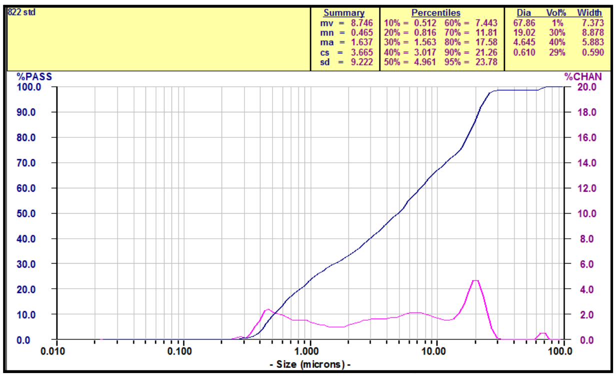
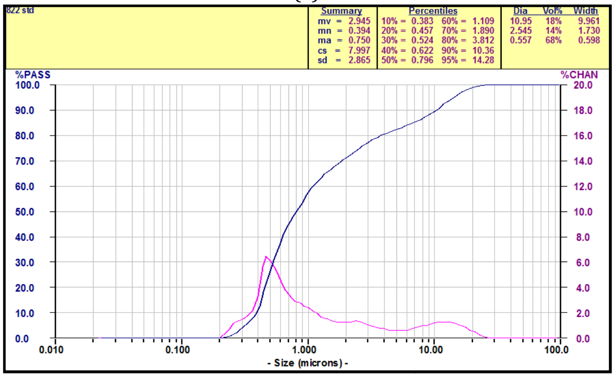
used in chlorination process, unless the size of these fines were enhanced by agglomeration.



(a)



(b)

Figure 2: (a) synthetic rutile fines (b) TiO_2 sludge

Crystallographic nature

The XRD spectrum of synthetic rutile fines and TiO_2 sludge were shown in Figure 3.

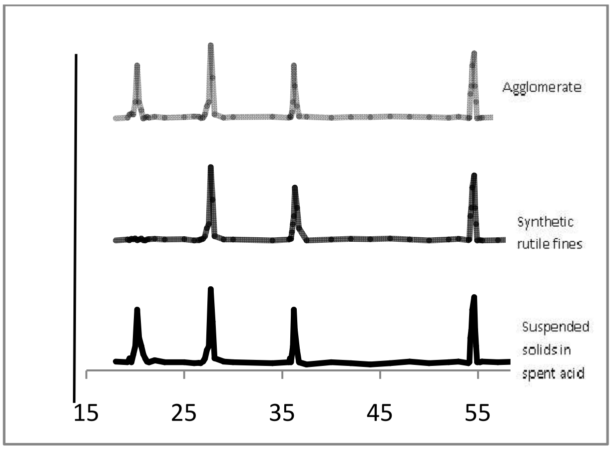
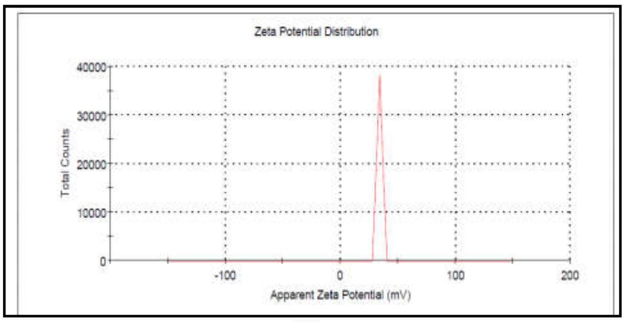


Figure 3: XRD pattern

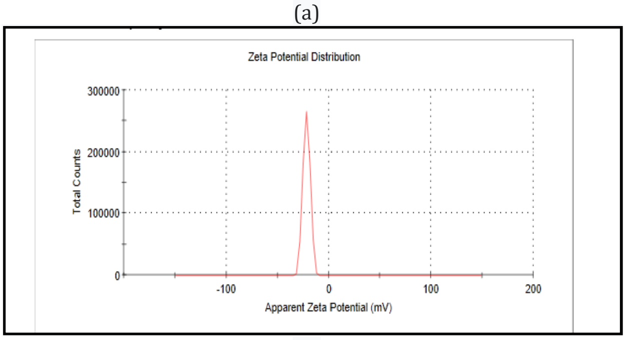
As expected, the synthetic rutile fines having a XRD peak as same as that of rutile peak (27.5^o, 36.2^o, 54.5^o).The XRD pattern of TiO_2 sludge, showed an additional peak at 20.26 ^{o}. This peak is due to the presence of hydrated TiO_2 present in the material. This hydrated TiO_2 was produced by the closed pressurized leaching of the ilmenite with HCl. The hydrated TiO_2 will have a surface charge, confirmed by zeta potential, which enhances the agglomerate formation.

Surface charge studies

The zeta potential curves of both synthetic rutile fines and TiO_2 sludge are shown in Figure 4(a) and 4(b). The zeta potential value of TiO2 sludge is +35 mV, where the zeta potential value of synthetic rutile fines was -21 mV. The zeta potential values between 0 to ±5 mV were having rapid coagulation tendency, the zeta potential lies between-10 to -35mV and +10 to +35 mV were having moderate coagulation tendency and zeta potential lies between -35 to -65 mV and +35 to +65 mV having poor coagulation tendency. The zeta potential of TiO_2 sludge and synthetic rutile fines were lies between -10 to -35 mV /+10 to +35 mV and it showed that both these material were having moderate coagulation tendency. The above study confirms that agglomeration is possible for these materials.



(a)



(b)

Figure 4: (a) Zeta potential ofTiO2 sludge, (b) zeta potential of Synthetic rutile fines

Production of green agglomerate

The synthetic rutile fines was mixed with a TiO_2 sludge approximately in 1:1 ratio in a agitator fabricated by in house development methods or a pan mixer. The agitator base rotates at a speed of 10 to 100 rpm. A racket shaped agitator was provided internally which revolves around 50 rpm. Baffles were provided at suitable locations inside the vessel, which ensures proper mixing of synthetic rutile fines with TiO_2 sludge and produces green agglomerate (GA)- Figure 5.

Figure 5: Photographs of Green agglomerate

Production of sintered agglomerate

The schematic representation of sintering process was given in Figure 6. The GA was subjected to a thermal treatment in a rotating kiln, along with LI produced from IBP plant in 1:1 ratio, at a temperature of 600 - 800 ^oC. The kiln is operated at a speed of 2 rpm. The residence time in the kiln was 2 hours. The outlet material from kiln was cooled by cooler which was operated by counter current flow of air. The cooler material was sieved in automatic vibrating screen of 2.0 mm mesh size to remove the larger material. The underflow obtained is the agglomerated sintered samples.

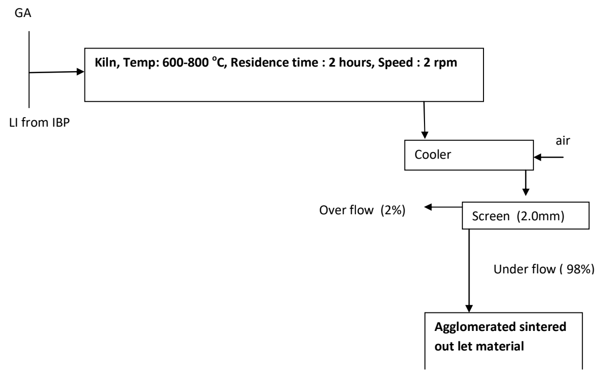


Figure 6: Schematic representation of sintering process

The products so formed were evaluated both for particle size and quality (TiO_2, Fe_2O_3 and SiO_2). The results are given in Table-3. The particle size enhancement was noticed during the thermal treatment. The under sized fraction (less than 100 micron) was found to be around 23 % at all the temperatures studied. The agglomeration/sintering was found to be occurred inside the kiln having temperature of 600 to 800 ^{o}C and a residence time of 2 hours. The synthetic rutile produced was having 77 % of particle size within the specification limit of synthetic rutile used for chlorination process in fluidized bed reactor. The TiO_2 content in the synthetic rutile agglomerate was above 93.0 %, with silica around 1.0 %, and Fe_2O_3 around 3.5%. The specification of synthetic rutile used for chlorination were having TiO_2 content of above 92%, silica content of less than 2% and iron oxide less than 5%. The synthetic rutile agglomerate produced meets the specification of the feed stock for chlorination process but the fines fraction of around 23 %, restricts its re-use as feed stock in chlorinator for producing titanium tetra chloride.

Table-3: Characterization of agglomerate obtained

Exp	Characterization of calcined samples							
	Temp.	Particle size (micron), %				Composition (%)		
	(oC)	420	150	100	< 100	TiO2	SiO2	Fe2O3
1	600	30.60	21.51	25.47	22.42	93.2	1.1	3.4
2	700	29.99	21.15	25.12	23.74	93.1	1.0	3.6
3	800	28.57	22.14	26.98	22.31	93.2	1.1	3.5

Theory

The synthetic rutile fines is having particle size less than 100 micron and apart from this, there is no quality difference between fines and synthetic rutile. Lower particle size of the fines restricts its use as feed stock in chlorination process. These fines generated by the aberration between particles during acid leaching. This fine behaves as free flowing material. On the other hand, the TiO_2 sludge in spent acid was produced by the hydrochloric acid leaching and carried over along with the spent acid after leaching. A small amount of TiO_2 in ilmenite also undergoes digestion in acid and produced titanium oxy chloride and hydrated titanium oxides. Hence the TiO_2 sludge in spent acid contains titanium oxy chloride, hydrated precipitate of titanium oxide and the leached ilmenite fines. This sludge was having surface charge and forms coagulated mass in spent acid. This sludge is separated from the spent acid by giving sufficient settling time and draining the bottom part. While mixing the synthetic rutile fines with TiO_2 sludge, the surface of the synthetic rutile fines will be soaked with the TiO_2 sludge particles. This will create a surface charge and particles tend to agglomerate and will form green agglomerate. This green agglomerate on heating at elevated temperature to form sintered agglomerate of required size. The green agglomerate alone was heated in a kiln, the attrition was found to be on the higher side creating more fines. By using LI mixed GA the attrition rate inside the kiln will be minimized. The schematic representation of theory of agglomeration was given in Figure 7.

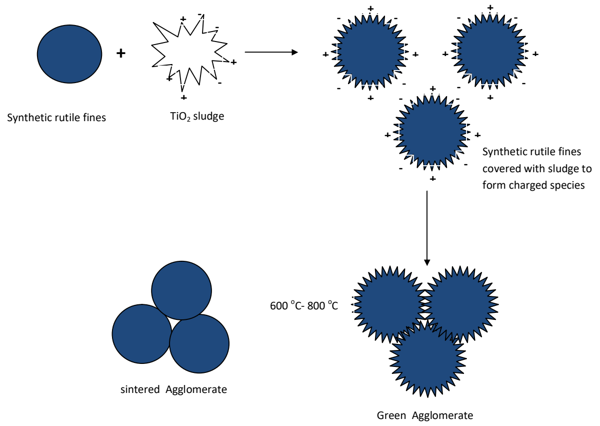


Figure 7: The schematic representation of theory of agglomeration

Conclusions

The present invention mainly relates to recover and re-use of synthetic rutile fines and TiO_2 sludge generated in the ilmenite beneficiation plant. The quantity of synthetic rutile fines and TiO_2 sludge produced were 1.0 MT and 3.0 MT/day respectively in a synthetic rutile production plant having the synthetic rutile production capacity of 140 MT/day. The synthetic rutile suitable for chlorination process under fluidized bed reactor was having a specification of TiO_2 content above 90 %, silica content less than 2 %, and particle size above 100 microns. The synthetic rutile fines and TiO_2 sludge were having same properties as that of synthetic rutile used in chlorination process except in particle size (the required particle size of synthetic rutile for chlorination is above 100 micron in size). The particle size for both fines and sludge are below 100 microns in size and hence these materials were not suitable for chlorination process. Presently these materials were treated as waste and goes along with ETP solid generated in the TiO_2 production plant. The agglomeration technology was successfully used to resize these materials suitable for chlorination process. By developing this technology, 4.0 MT of the synthetic rutile production will be increased per day. Moreover, the quantity of ETP solid generation is also decreased.

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