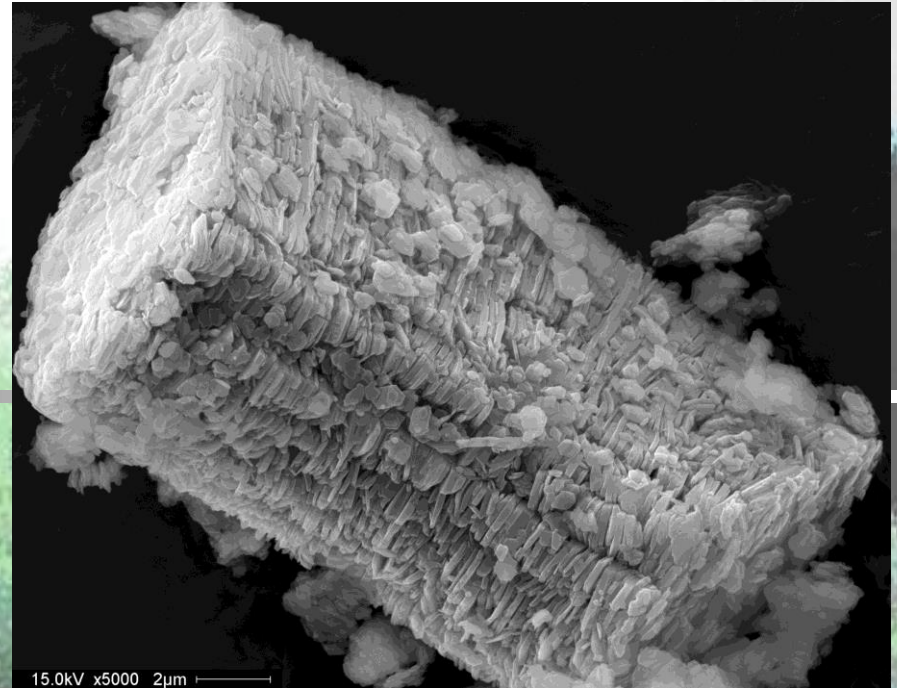
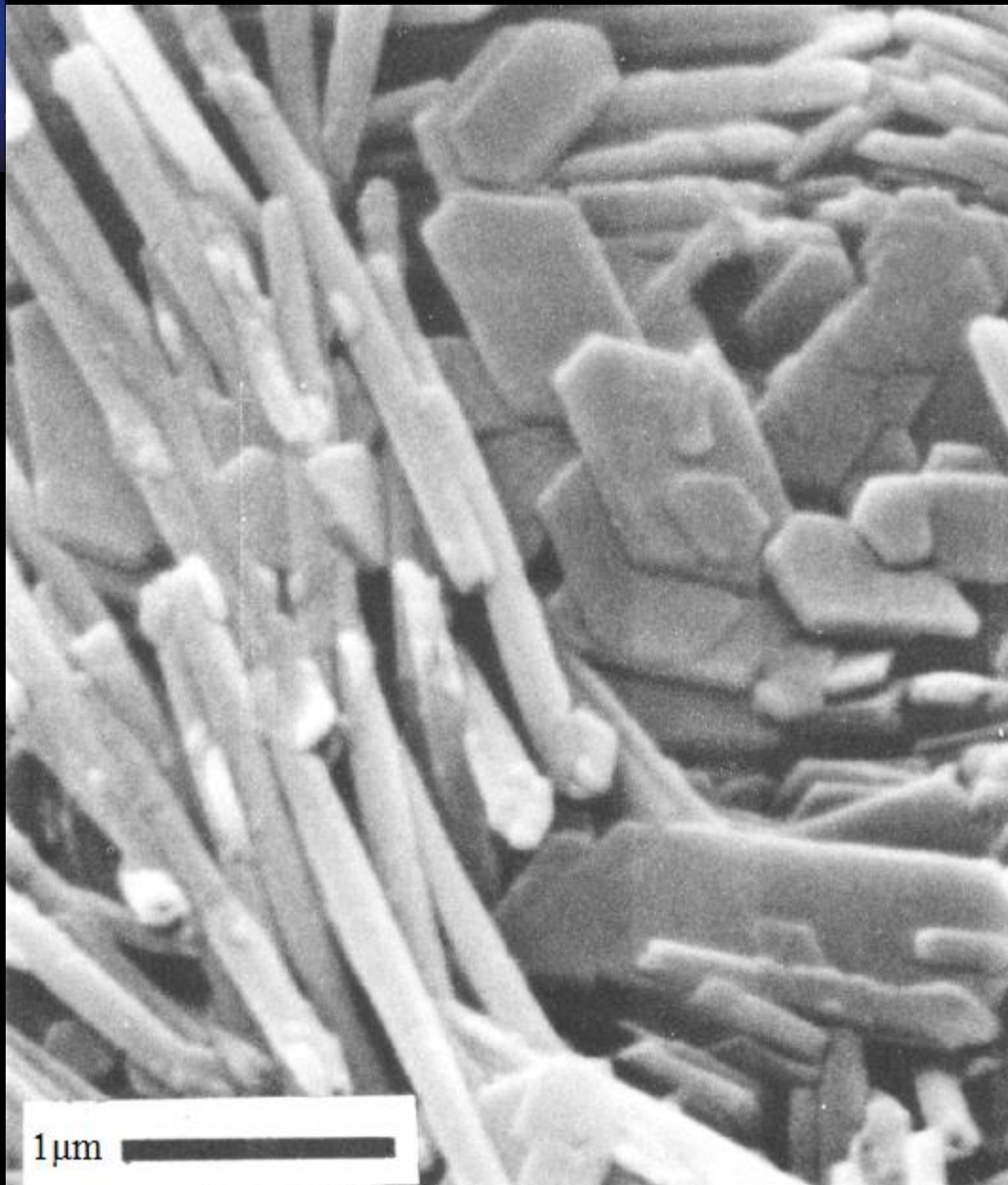


Aula 7 – Caulins : Usos Industriais



PMT 5846 – Ciência e Tecnologia de Argilas

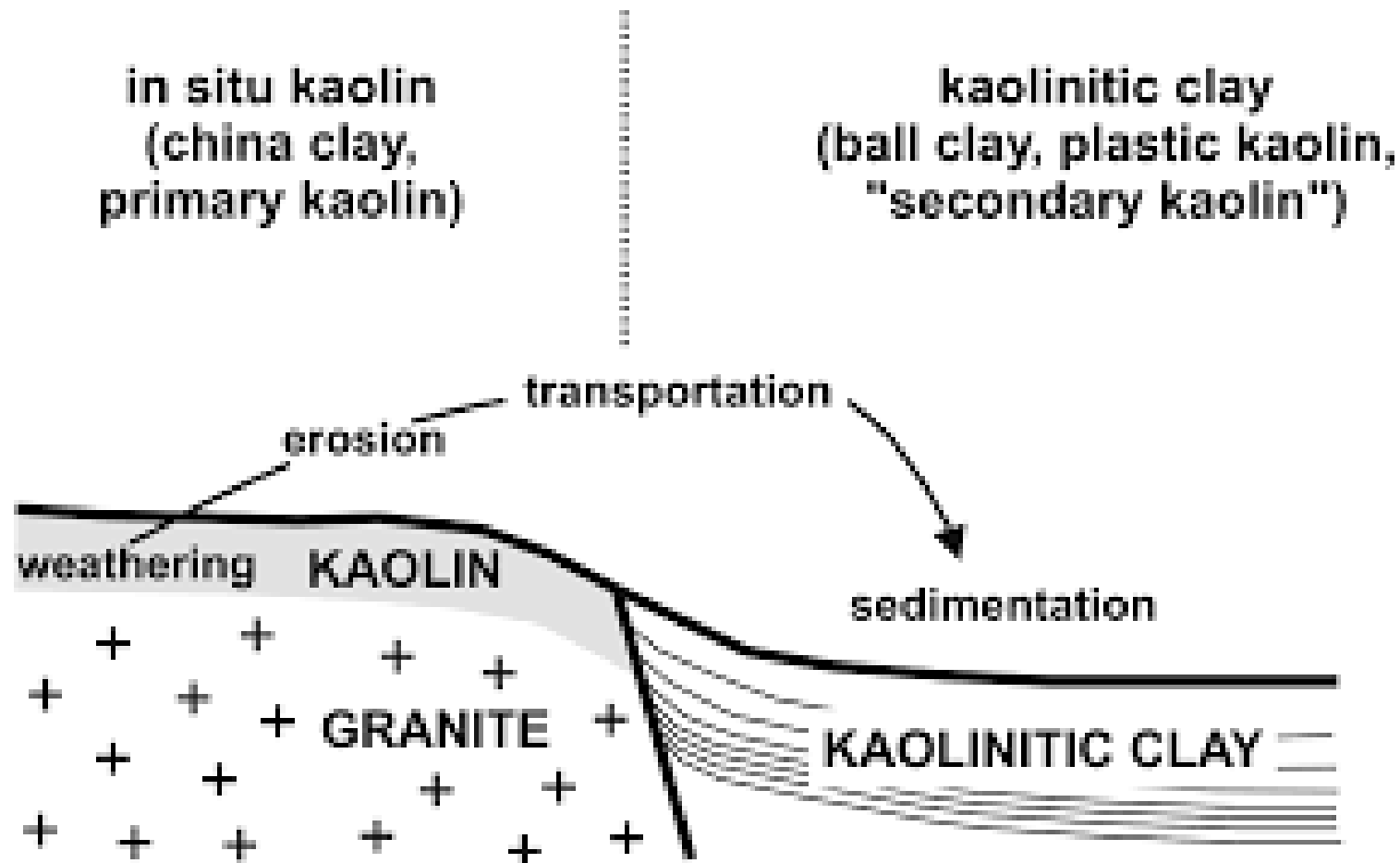
Prof. Antonio Carlos Vieira Coelho
Departamento de Engenharia Metalúrgica e de Materiais
EPUSP - 2020



*Scanning electron micrograph
of sample 5
(Suzhou, Jiangsi Province),
showing elongate crystals
and plates in sharp, immediate
micro-contact.
Note the two distinct
morphologies*

*Keller, Cheng, Johns, Meng.
Kaolin from the original Kauling (Gaoling)
Mine locality, Kiangsi Province, China.
Clays and ClayMinerals 28 (2), 97-104 (1980)*

Caulins Primários e Secundários: Origens Geológicas





Propriedades Industriais dos Caulins

Table 11. Important properties of kaolin

1	White or near-white in color
2	Chemically inert over a wide pH range (4–9)
3	Fine in particle size
4	Soft and non-abrasive
5	Platy with the plate surface dimensions relatively large compared to the thickness
6	Hydrophilic and disperses readily in water
7	Because of its shape, it has good covering and hiding power when used as a pigment or extender in coatings
8	Plastic, refractory and fires to a white or near-white color
9	Low conductivity of both heat and electricity
10	A very low charge on the lattice
11	A low surface area as compared with other clay minerals
12	Some kaolins have a low viscosity and flow readily at 70% solids
13	Relatively low in cost



Propriedades Físicas dos Caulins

Table 12. Representative physical constants of kaolinite

Specific gravity	2.62
Index of refraction	1.57
Hardness (Mohs' scale)	1.5–2.0
Fusion temperature (°C)	1850
Einlehner abrasion number	4–10
Dry brightness at 457 nm (%)	75–93
Crystal system	Triclinic

2.5. Measurement of abrasivity

The abrasivity by bentonite dispersions was determined by the mass loss (mg) of a bronze wire before and after rotation in the bentonite dispersion using an Einlehner AT 1000 apparatus (Fig. 2). First, the initial weight of the clean and dry wire was determined before the measurement. Then 10 g bentonite (dried at 105 °C, as required in the industrial standard test) were dispersed in 1000 g deionised water for 10 min at 3000 rpm. The abrasion was measured 1 h after dispersion. The wire was assembled into the Einlehner apparatus with dispersion. After stirring for 174,000 rotations (= 2 h) the mass loss of the cleaned and dried wire was measured.

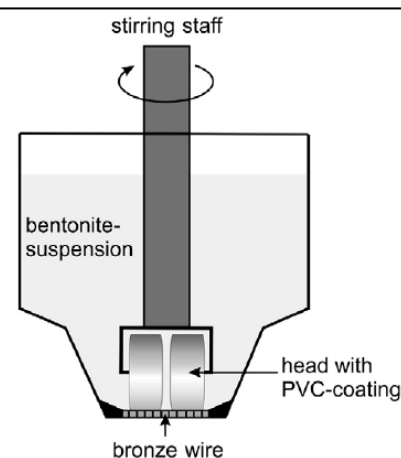


Fig. 2. Principal sketch of abrasion tester Einlehner AT 1000.

ABRASIVIDADE:
KLINKENBERG et al. *Applied Clay Science* 46, 37-42 (2009).



Usos Industriais dos Caulins

Table 2. Industrial uses of kaolin

Paper coating	Cement	Food additives
Paper filling	Pencil leads	Bleaching
Extender in paint	Adhesives	Fertilizers
Ceramic raw material	Tanning leather	Plaster
Filler in rubber	Pharmaceuticals	Filter aids
Filler in plastics	Enamels	Cosmetics
Extender in ink	Pastes and glues	Crayons
Cracking catalysts	Insecticide carriers	Detergents
Fiberglass	Medicines	Roofing granules
Foundries	Sizing	Linoleum
Desiccants	Textiles	Polishing compounds

KAOLIN SOLD OR USED BY PRODUCERS IN THE UNITED STATES, BY USE¹

(Thousand metric tons)

MYB2012

MYB2013

Usos Industriais
do Caulim
EUA

Use	2011	2012	2012	2013
Domestic:				
Ceramics:				
Catalyst (oil and gas refining)	162	252	189 ^r	175
Fine china and dinnerware	6	7	7	8
Floor and wall tile	93	82	82	55
Pottery ²	W	W	W	W
Roofing granules	27	15	31 ^r	33
Sanitaryware	27	21	41 ^r	44
Miscellaneous	681 ^r	605	369 ^r	515
Chemical manufacture	W	W	W	W
Fiberglass, mineral wool	279	261	306 ^r	307
Fillers, extenders, binders:				
Adhesive	37 ^r	31	31	39
Paint	190 ^r	256	256	287
Paper coating	1,630 ^r	1,190	1,190	1,410
Paper filling	130	181	181	221
Pesticide ²	W	W	W	W
Plastic	45 ^r	52	53 ^r	61
Rubber	143 ^r	129	175 ^r	263
Miscellaneous	86	103	68 ^r	31
Heavy-clay products:				
Brick, common and face	25	23	23	26
Portland cement	64	13	50 ^r	68
Refractories ³	701	719	719	609
Miscellaneous applications	105 ^r	58	151 ^r	85
Total	4,430 ^r	4,000	3,930 ^r	4,240
Exports, reported by producers:				
Ceramics ²	W	W	W	W
Paint	62 ^r	124	123 ^r	125
Paper coating	1,210 ^r	1,280	1,280	1,150
Paper filling	46	231	W	W
Rubber	69 ^r	86	86	45
Miscellaneous	137 ^r	252	486 ^r	393
Total	1,520 ^r	1,980	1,980 ^r	1,710
Grand total	5,950 ^r	5,980	5,900 ^r	5,950

^rRevised. W Withheld to avoid disclosing company proprietary data.

¹Data are rounded to no more than three significant digits; may not add to totals shown.

²Included in "Miscellaneous."

³Includes firebrick (blocks and shapes), grogs and calcines, and miscellaneous refractories.



Caulim – Exportação (EUA)

TABLE 14
U.S. EXPORTS OF CLAYS, BY TYPE¹

(Thousand metric tons and thousand dollars)

Type of clay	2012		2013		Principal destinations in 2013
	Quantity	Value ²	Quantity	Value ²	
Ball clay	77 ¹	4,580	52	6,610	Belgium, 70%; Nicaragua, 15%; Japan, 13%; Costa Rica, 11%.
Bentonite	1,030 ¹	164,000 ¹	890	157,000	Canada, 49%; Japan, 11%; China, 6%.
Fire clay	289	47,200	268	41,100	Mexico, 44%; Luxembourg, 20%; Japan, 11%; Netherlands, 5%.
Fuller's earth	107 ¹	36,300 ¹	86	29,100	Japan, 70%; Brazil, 9%; Italy, 8%; China, 6%; Netherlands, 6%.
Kaolin	2,450	549,000	2,540	577,000	Taiwan, 70%; Mexico, 10%; Japan, 10%; Korea, Republic of, 10%.
Clays ³	315 ¹	68,200 ¹	304	81,200	Japan, 70%; Mexico, 20%; Germany, 5%; Korea, Republic of, 4%.
Total	4,270 ¹	870,000 ¹	4,140	892,000	

¹Revised.

¹Data are rounded to no more than three significant digits; may not add to totals shown.

²Free alongside ship.

³Not elsewhere classified.

Source: U.S. Census Bureau.



Caulim – Importação (EUA)

TABLE 15
U.S. IMPORTS FOR CONSUMPTION OF CLAY, BY TYPE¹
(Thousand metric tons and thousand dollars)

Type of clay	2012		2013		Principal sources in 2013
	Quantity	Value ²	Quantity	Value ²	
China clay or kaolin	472	56,800	468	56,000	Brazil, 96%.
Fire clay	8	1,380	3	1,390	China, 82%; United Kingdom, 7%; Hong Kong, 4%.
Ball clay	(3)	137	(3)	174	United Kingdom, 67%; China, 24%; Canada, 5%; Brazil, 4%.
Bentonite	12	15,300	15	16,100	Mexico, 32%; China, 27%; Egypt, 18%; United Kingdom, 16%.
Fuller's earth	1	160	8	434	China, 55%; Japan, 34%; Canada, 11%.
Chamotte or Dina's Earth	(3)	109	(3)	159	United Kingdom, 90%; Germany, 10%.
Artificially activated clay and earth	31	34,000	28	31,500	Mexico, 34%; Germany, 18%; China, 18%; Belgium, 14%.
Total	524	108,000	523	106,000	

¹Data are rounded to no more than three significant digits; may not add to totals shown.

²Customs value.

³Less than ½ unit.

Source: U.S. Census Bureau; data adjusted by U.S. Geological Survey.



Caulim – Produção Mundial por País

TABLE 17
KAOLIN: WORLD PRODUCTION, BY COUNTRY OR LOCALITY¹ (Metric tons)

Country or locality ²	2012	2013	2014	2015	2016
Albania	961,000	768,000	810,000	1,161,000	1,160,000 ^e
Algeria	100,970	42,504	181,068	192,000 ^e	192,000 ^e
Argentina	66,574	77,063 ^r	46,400 ^{r,e}	61,000 ^{r,e}	61,000 ^e
Australia	89,229	204,521	172,000 ^{r,e}	260,000 ^{r,e}	260,000 ^e
Austria	43,174	40,055	36,334	32,126	32,000 ^e
Bhutan	7,353	15,166	10,209	--	-- ^e
Bosnia and Herzegovina	149,495	44,940	21,610	252,268	253,000 ^e
Brazil	2,189,000	2,200,000	2,055,000	2,100,000 ^e	2,100,000 ^e
Bulgaria	252,100	281,600	321,700	--	-- ^e
Cameroon	8,922	12,107	22,042	22,000	22,000 ^e
Chile	60,429	60,000	60,000 ^e	60,000 ^e	60,000 ^e
China ^e	3,300,000	3,300,000	3,200,000	3,200,000	3,200,000
Cuba	4,000	3,600	1,700	1,500	1,500 ^e
Czechia	3,318,000	3,108,000	3,281,000	3,454,000	3,500,000 ^e
Ecuador	42,564	100,195	40,236	63,829	64,000 ^e
Egypt	300,000 ^e	300,000 ^e	300,000 ^e	232,351	232,000 ^e
Eritrea ^e	-- ^r	-- ^r	-- ^r	-- ^r	--
Estonia	98,600	99,000	107,000	58,000	58,000 ^e
Ethiopia ³	4,200 ^e	4,400 ^e	4,530	4,600 ^e	4,600 ^e
France, marketable	315,000 ^e	267,000	317,000	320,000 ^e	320,000 ^e
Germany	4,398,796	4,290,000	4,275,000	4,300,000 ^e	4,300,000 ^e
Greece	6,268	--	--	--	-- ^e
Guatemala	1,866	2,953	1,285	1,100 ^{r,e}	1,100 ^e
Hungary, beneficiated	--	36 ^r	196 ^r	1,119 ^r	1,100 ^e

India: ^e					
Marketable crude	2,350,000 ^r	4,070,000 ^r	4,580,000 ^r	4,040,000 ^r	4,110,000
Processed	99,800 ^r	67,900 ^r	86,400 ^r	73,600 ^r	74,000
Indonesia ^e	180,000	180,000	180,000	180,000	180,000
Iran	800,000	946,388 ^r	820,067 ^r	791,193 ^r	790,000 ^e
Iraq	3,000	--	--	--	-- ^e
Italy ^e	8,000	8,000	8,000	8,000	8,000
Japan ^e	13,000	12,000 ^r	12,000 ^r	12,000 ^r	12,000
Jordan	76,194	80,000 ^e	80,000 ^e	80,000 ^e	80,000 ^e
Kenya ^e	1,000	1,100	1,600	1,800 ^r	1,800
Korea, Republic of	514,841	532,050	429,081	357,000 ^{r,e}	357,000 ^e
Kosovo	55,300	50,100	55,300	61,300	62,000 ^e
Kyrgyzstan	113,900	133,500	1,121,800	1,332,600	1,330,000 ^e
Lithuania	300,075	318,733	294,386	326,276	326,000 ^e
Madagascar	230	200	221 ^r	220 ^{r,e}	220 ^e
Malaysia	424,622	263,339	207,694	255,448	284,000 ^e
Mexico	163,148	379,110	342,917	320,078	330,000 ^e
New Zealand	11,578	13,066	61,382	13,659	14,000 ^e
Nigeria	15,420	17,000	19,200	22,000	24,100 ^e
Norway	225,000	225,000	225,000	225,000	225,000 ^e
Oman	139,500	114,678	67,000	169,500	170,000 ^e
Pakistan	22,000 ^r	16,463 ^r	13,803	23,100 ^{r,e}	23,100 ^e
Peru	34,585	32,249	19,964	43,500 ^{r,e}	19,300 ^e
Philippines	4,631 ^r	6,568	7,050	8,180 ^{r,e}	8,200 ^e
Poland:					
Crude	249,000	268,000	278,000	287,000	290,000 ^e
Beneficiated	138,000	166,000	164,000 ^e	169,000 ^e	170,000 ^e
Portugal, washed and unwashed	321,039	248,008	269,073	260,000 ^e	260,000 ^e
Romania	--	32,722	30,638	31,000 ^e	31,000 ^e
Russia ^e	284,000 ^r	674,000 ^r	787,000 ^r	786,000 ^r	786,000
Saudi Arabia	137,000	101,000	106,000	120,000	120,000 ^e
Serbia	155,000	156,000	214,000	216,210	217,000 ^e



Caulim – Produção Mundial por País - **FINAL**

Country or locality ²	2012	2013	2014	2015	2016
Slovakia	3,000 ^e	6,000 ^e	6,000 ^e	10,502 ^r	11,000 ^e
South Africa	20,791	22,295	27,258	20,150	21,100 ^e
Spain, marketable, crude and washed	247,000	247,000 ^e	247,000 ^e	247,000 ^e	247,000 ^e
Sri Lanka	11,800 ^{r,e}	13,000 ^{r,e}	13,000 ^e	13,500 ^e	13,500 ^e
Sudan	11,579	26,000	33,770	14,490	15,000 ^e
Taiwan	26,376	15,963	1,808	732	4,040 ^e
Tanzania	1,422 ^r	907 ^r	3,809	1,953	2,000 ^e
Thailand:					
Filler	300	--	--	--	-- ^e
Nonbeneficiated	1,000,975	631,133	755,913	655,196	655,000 ^e
Turkey	988,081	1,168,441	2,032,103	1,887,302	1,900,000 ^e
Uganda	42,886	43,875	46,286	34,700 ^{r,e}	34,000 ^e
Ukraine	1,218,000	1,179,000	1,426,000	1,815,000	1,820,000
United Kingdom ^e	1,150,000	1,110,000	1,090,000	1,010,000	1,010,000
United States	5,720,000 ^r	5,880,000 ^r	6,020,000 ^r	5,810,000 ^r	5,320,000 ^e
Uzbekistan	300,000 ^e	70,286	64,605	304,000 ^{r,e}	304,000 ^e
Venezuela	2,447	2,793	2,500	2,400 ^e	2,400 ^e
Total	33,300,000 ^r	34,700,000 ^r	37,500,000 ^r	37,800,000 ^r	37,500,000

^eEstimated. ^rRevised. -- Zero.

¹Table includes data available through November 23, 2017. All data are reported unless otherwise noted. Totals, U.S. data, and estimated data are rounded to no more than three significant digits; may not add to totals shown.

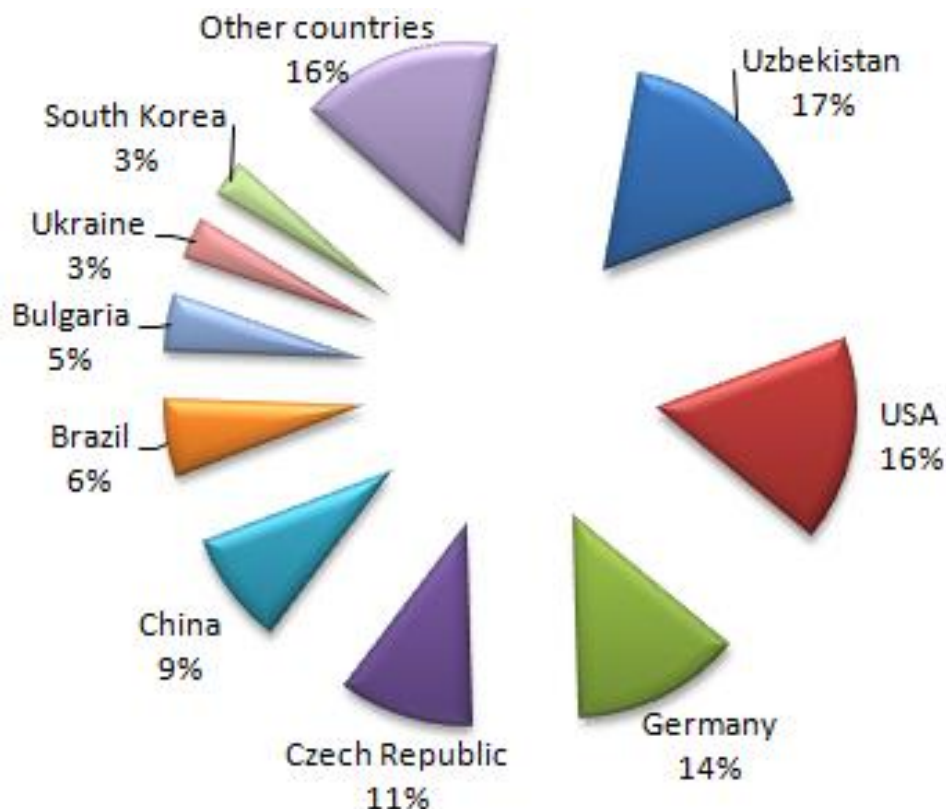
²In addition to the countries and (or) localities listed, Belgium, Denmark, Nigeria, Paraguay, Vietnam, and Zambia produced kaolin, but available information was inadequate to make reliable estimates of output levels.

³Production is based on fiscal year, with a starting date of July 7.

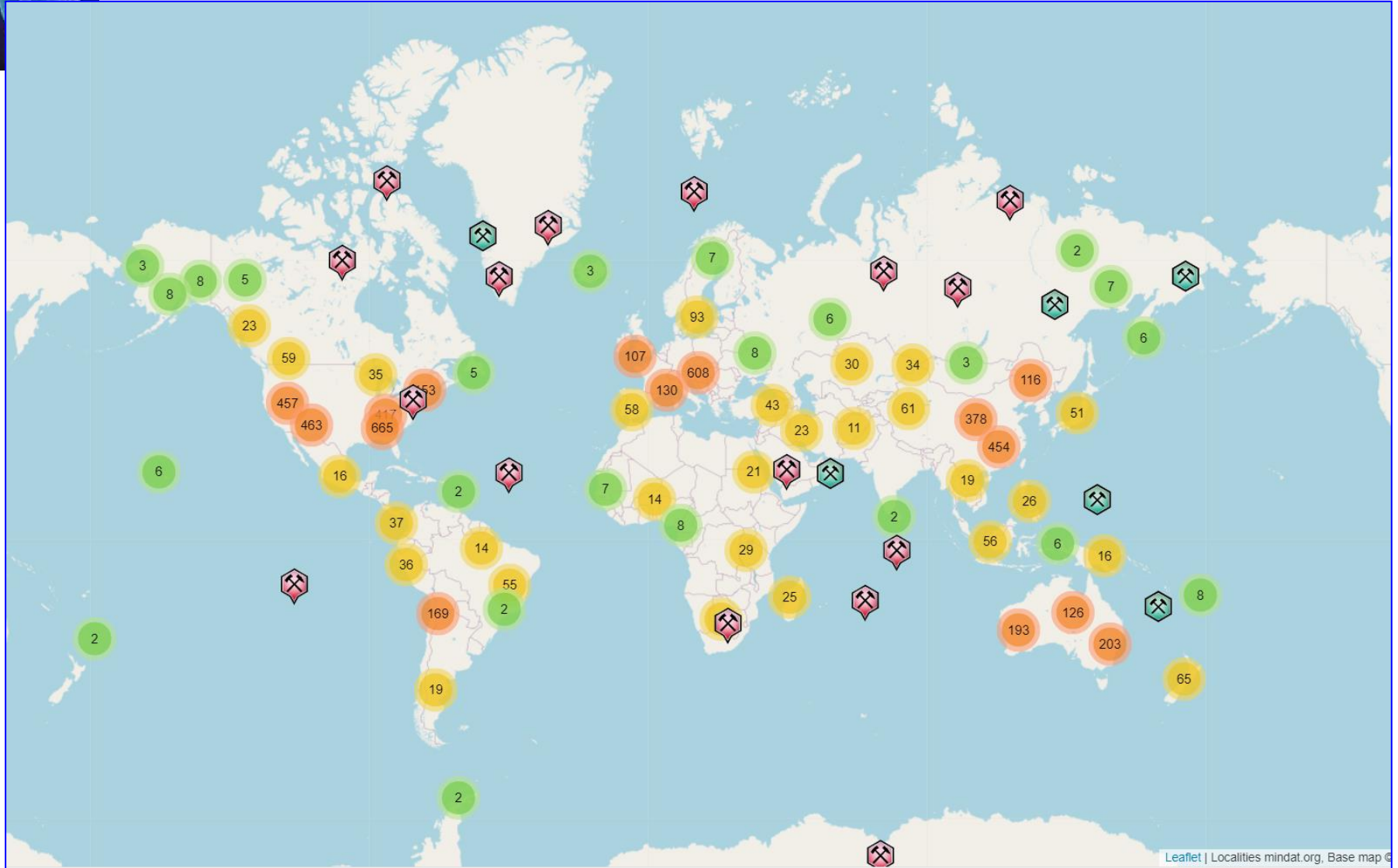


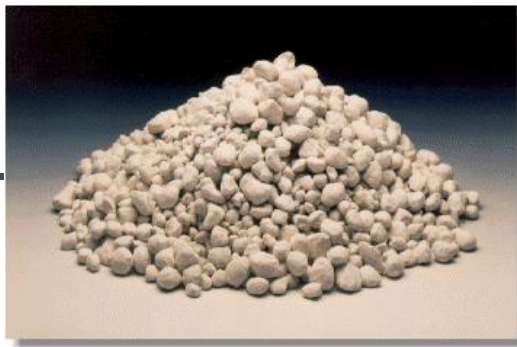
Produção de Caulim no Mundo

- Uzbequistão
 - Angren
- Estados Unidos
 - Georgia; South Carolina
- Alemanha
 - Bavária
- República Tcheca
 - Região de Karlovy Vary
- China
 - Suzhou (*província de Jiangsu*)
- Inglaterra
 - Cornwall; Devon

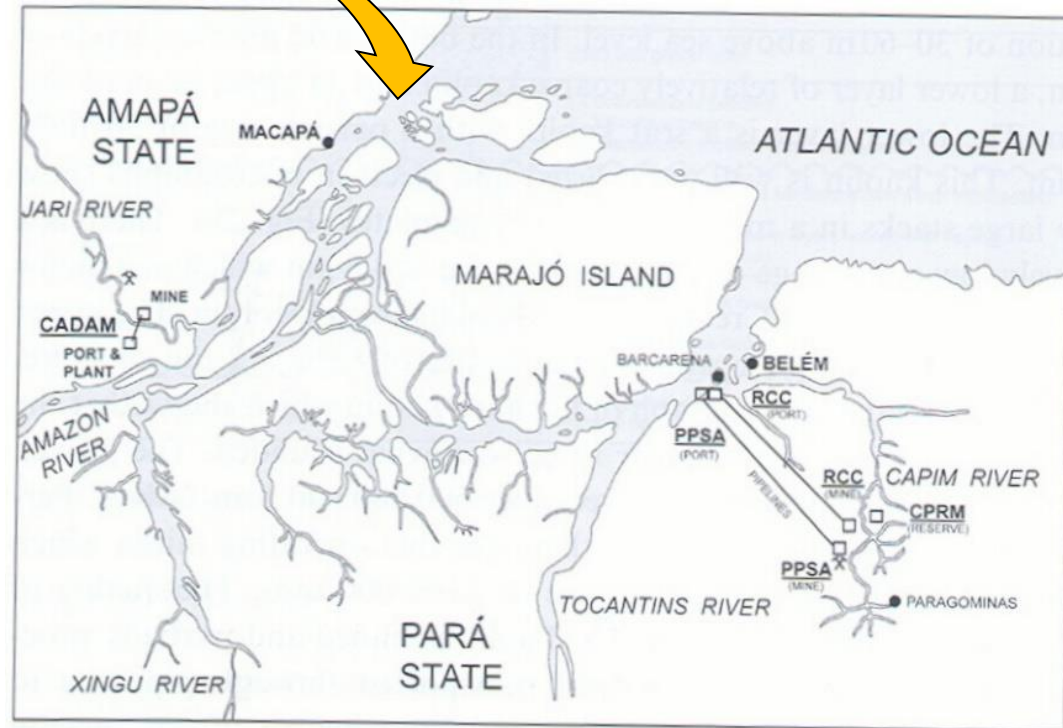
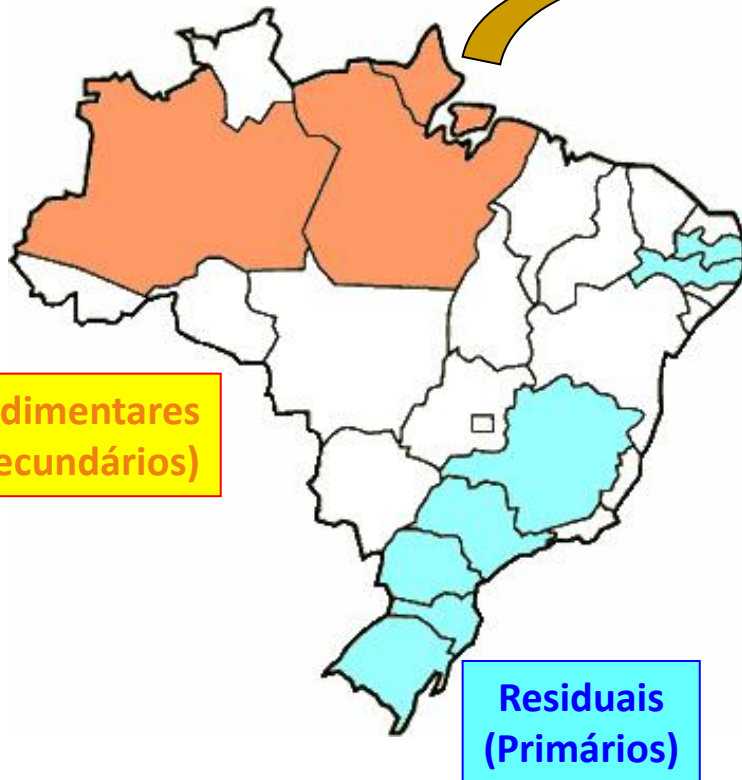


Caulinita no Mundo





Caulins no Brasil



Location of kaolin mines and plants in northern Brazil.



Caulins no Brasil

FIG. 2. Kaolin deposits of Brazil.

Caulins no Brasil



Figura 7: MET de caulim Haloisítico de Juiz de Fora, Minas Gerais.

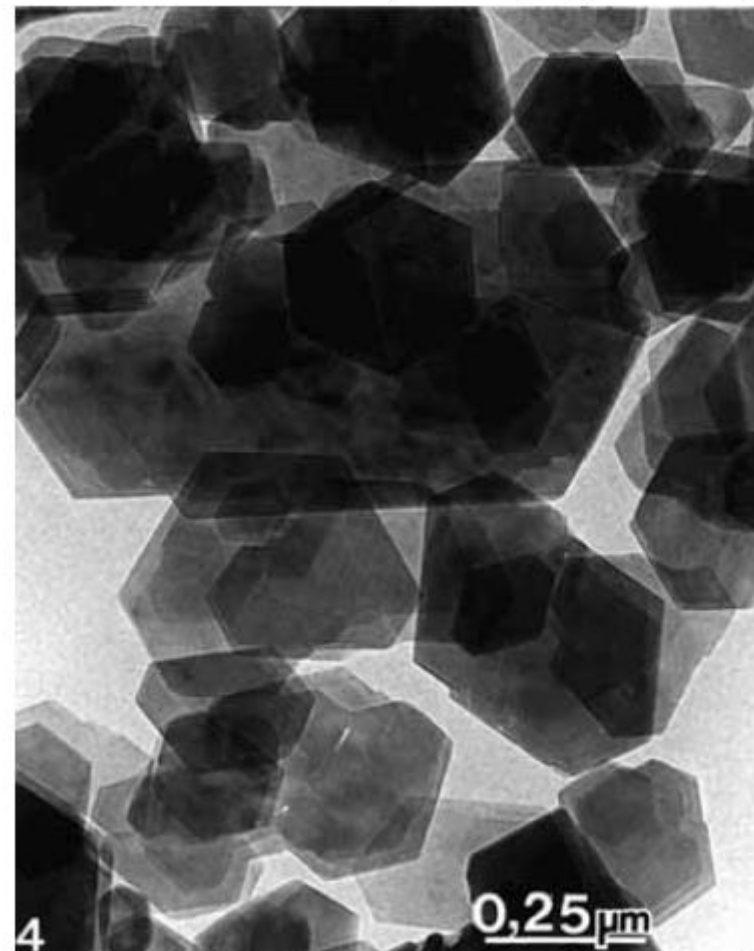


Figura 4: Micrografia eletrônica de transmissão (MET) do caulim caulínítico "Amazon 88" da CADAM-Rio Jari, Território do Amapá.

WILSON, I. et al. *Cerâmica* 44, 118-139 (1998).



Usos Industriais do Caulim

Maior Uso Industrial do Caulim

- a. O maior uso industrial do caulim é para a **fabricação de papel**, com um detalhe: são dois tipos de uso:
 - para cobertura ou revestimento externo do papel (“**paper coating**”)
 - para carga ou enchimento do papel (“**paper filling**”)
- b. Portanto, em primeiro lugar os ensaios tecnológicos devem avaliar se o caulim é de um tipo ou de outro.
- c. Todos os ensaios tecnológicos do caulim, a começar para aplicação para papel (a mais importante industrialmente), devem ser feitos com a fração argila (FA) de um caulim.

- a. A seguir são descritas as etapas a serem seguidas para a separação da “fração argila (FA)” de uma amostra de argila.
 - b. Esquemas da produção de caulins para cobertura e carga são mostrados a seguir; são mostradas também fotografias de minas em operação.



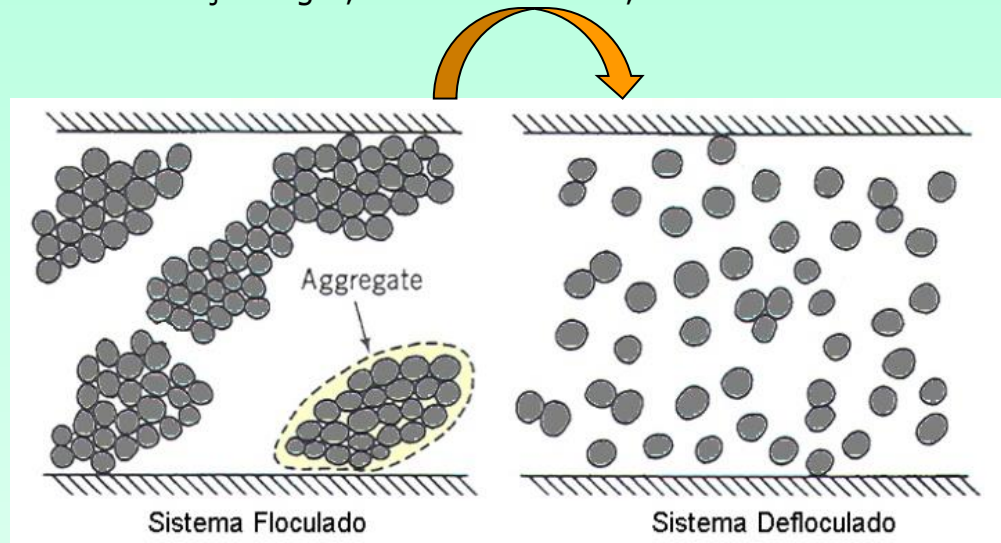
Determinação da Fração Argila

- Um procedimento experimental possível é o seguinte:
 - Pesar 20 gramas da argila, com a umidade previamente medida. Colocá-las em um recipiente de aço inoxidável de 1 litro.
 - Colocar 500mL de água filtrada ou destilada.
 - Adicionar 5 miliequivalentes de Na^+ (presente em carbonato de sódio); agitar o sistema.
 - $5\text{mEq } \text{Na}^+ = 265\text{mg } \text{Na}_2\text{CO}_3$, que correspondem a 355mg de $\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ ou 715 mg de $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.
 - Deixar em repouso à temperatura ambiente por 12 a 24 horas, para hidratação dos argilominerais e da matéria orgânica porventura existente.
 - No dia seguinte, aquecer o recipiente à ebulição por uma hora, com agitação periódica.
 - Deixar esfriar e transferir para o copo de um liquidificador (comum, do tipo dos utilizados em cozinha), com um mínimo de água de lavagem.
 - Ligar o liquidificador com velocidade média por meia hora.

Determinação da Fração Argila *(cont.)*

- Passar o conteúdo do copo em peneiras ABNT nº100 e nº325, coletando a suspensão que passa pela peneira nº325, que contém a "Fração Argila (FA)".
- Examinar com lupa (aumento 10X) as impurezas retidas nas peneiras nº100 e nº325 para verificar se ainda contém argila.
 - Se não contiver, esta fase, de peneiramento, está encerrada.
 - **Caso contenham argila**, as peneiras devem ser secas à temperatura ambiente até que todo o seu conteúdo possa ser coletado como um pó. Este é colocado em um almofariz de porcelana e levemente triturado ou atritado (não moído) para tentar facilitar a liberação da argila aderida às partículas de impureza. **Repetir** o tratamento anterior com a mesma massa de carbonato de sódio. Coletar a Fração Argila, se ela for liberada, e encerrar essa fase do tratamento.

*Na⁺ é colocado para **deflocular** o sistema → isso é feito para aumentar a separação de finos do material*





Determinação da Fração Argila *(cont.)*

- O objetivo da adição do carbonato de sódio é o de favorecer a criação da dupla camada iônica difusa de Gouy-Chapman-Stern nos argilominerais e nos minerais acessórios e fazer com que os ácidos húmico e fúlvico da matéria orgânica tenham a forma solúvel em água → *facilitar a defloculação e dispersão das partículas de argilomineral.*
- Os resíduos em peneira são secos à temperatura ambiente ou abaixo de 50°C para evitar deformações nas aberturas. A porcentagem em peso de impurezas retidas a úmido na peneira ABNT nº325 é calculada pela fórmula:

$$\% \text{ impurezas } (\varphi < n^{\circ} 325) = \frac{\text{peso seco dos resíduos } n^{\circ} 100 \text{ e } n^{\circ} 325}{\text{peso seco das 20g (secas a } 105^{\circ} \text{C} - 110^{\circ} \text{C)}} \times 100$$

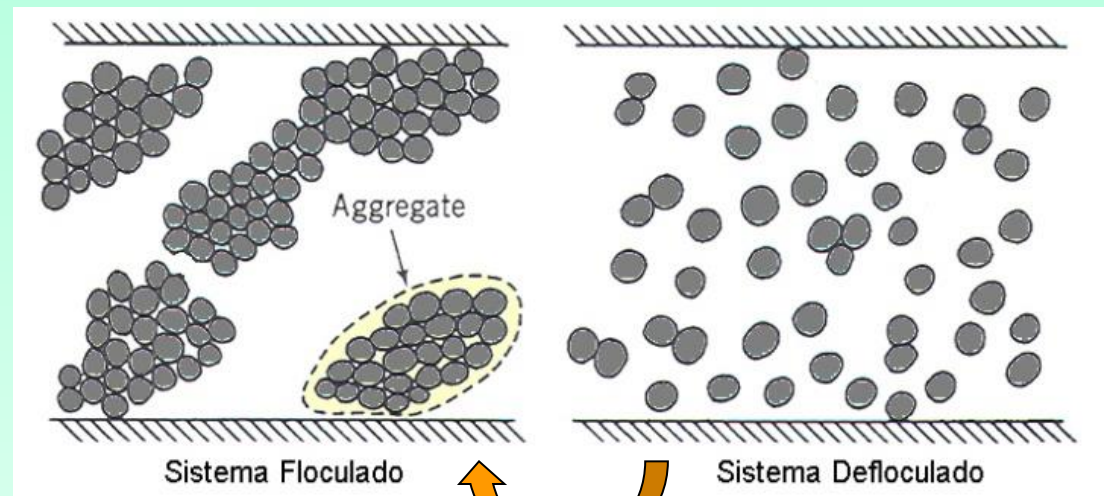
- A diferença [100% - %impurezas] é igual à porcentagem de (argilominerais + impurezas) com diâmetro menor que 44µm (abertura da peneira nº325).



Determinação da Fração Argila (cont.)

- A dispersão é floculada (precipitada ou coagulada) com solução de cloreto de cálcio 1M, que é adicionado até que seja observado o final da precipitação; agitar e deixar sedimentar.
- Transferir, quantitativamente, o precipitado para um saco de celofane para diálise; dialisar contra água destilada até reação negativa de íon cloreto.
- Secar o saco de diálise a 70°C e transferir o pó, quantitativamente, para secagem a 105°C/110°C. Pesar o resíduo.

Ca^{2+} é colocado para **flocular** o sistema → isso é feito para facilitar a recuperação das partículas de argilominerais, minimizando perdas de finos do material





Determinação da Fração Argila *(final)*

- Se **P** for o peso das 20 gramas secas a 105°C/110°C e **R** for o peso do resíduo com partículas de dimensões menores que 44µm, floculado e seco a 105°C/110°C, então a “% de Fração Argila” = **F_(%)** será dada por:
 - **F_(%)** = [**R/P**] x 100 é a porcentagem de (argilominerais+impurezas) com diâmetro menor que 44µm que a argila original contém.
- A partir do resultado de **F_(%)** poderá ser pensada uma aplicação industrial para a argila original – *se o valor for muito baixo, mesmo que a argila tenha propriedades interessantes, o emprego industrial pode ser inviabilizado.*
- A partir do material que constitui o resíduo em pó (que será chamado a seguir de **FA**, “Fração Argila”) poderão ser obtidos resultados preliminares sobre os prováveis grupos de argilominerais constituintes da argila original e uma provável indicação, a partir de ensaios tecnológicos, do tipo de Argila Industrial no qual poderá ser classificada a argila original.



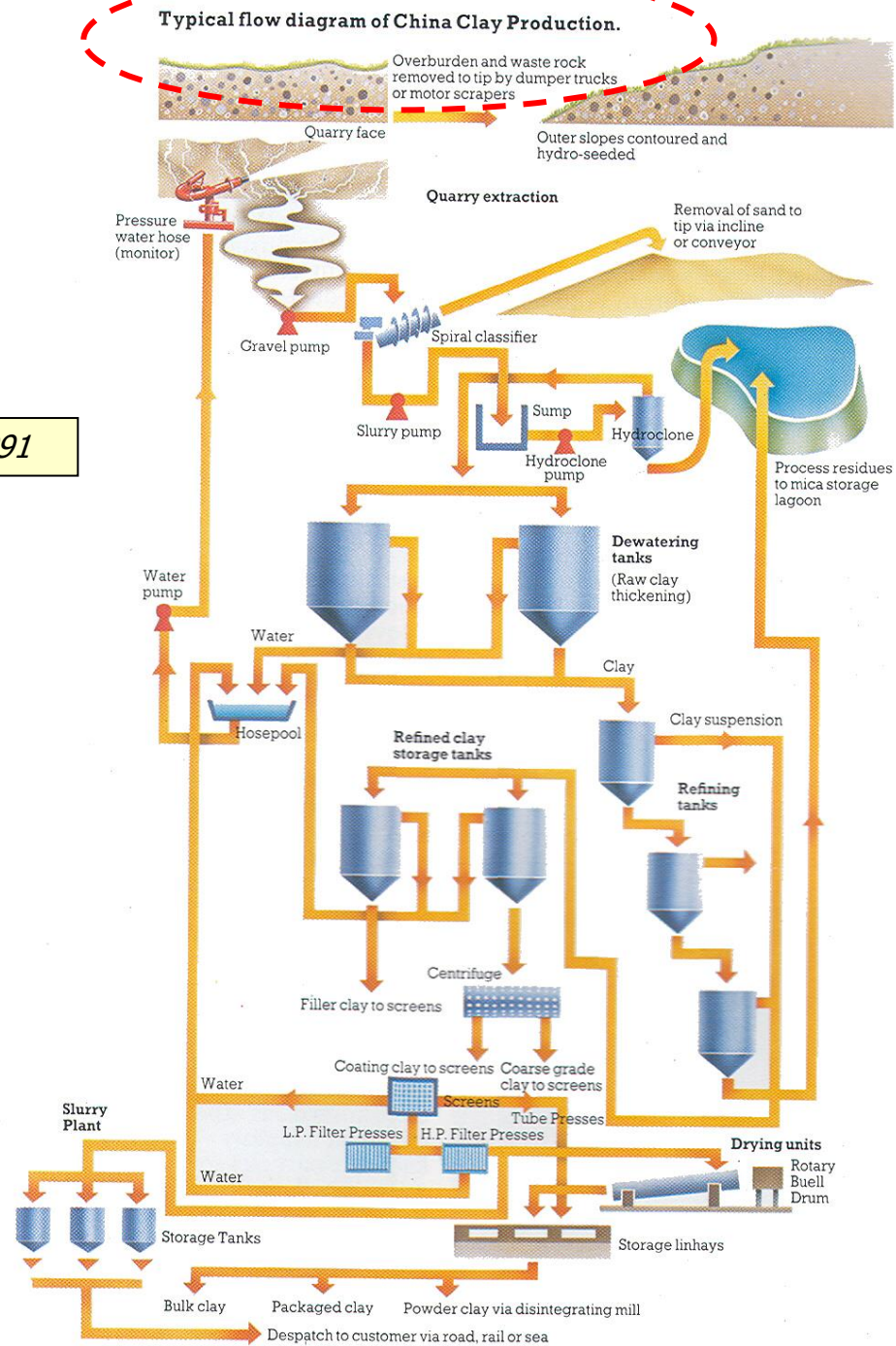
Usos Industriais do Caulim

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 - para carga ou enchimento do papel (“paper filling”)
- b. Portanto, em primeiro lugar os ensaios tecnológicos devem avaliar se o caulim é de um tipo ou de outro.
- c. Todos os ensaios tecnológicos do caulim, a começar para aplicação para papel (a mais importante industrialmente), devem ser feitos com a “fração argila (FA)” de um caulim.
 - a. A seguir são descritas as etapas a serem seguidas para a separação da fração argila (FA) de uma argila.
 - b. **Esquemas da produção de caulins para cobertura e carga são mostrados a seguir; são mostradas também fotografias de minas em operação.**



ECHO Magazine, ECC, p.6, 1991





Reino Unido



*ECHO Magazine,
ECC, p.7, 1991*



Reino Unido



Aerial image of China Clay (Kaolin) Quarries, St. Austell, Cornwall, UK



Reino Unido



Above High pressure water is used to wash kaolin (china clay) from altered (kaolinised) granite in the St Austell area of Cornwall.

*caulim **primário** ou **residual***



República Tcheca



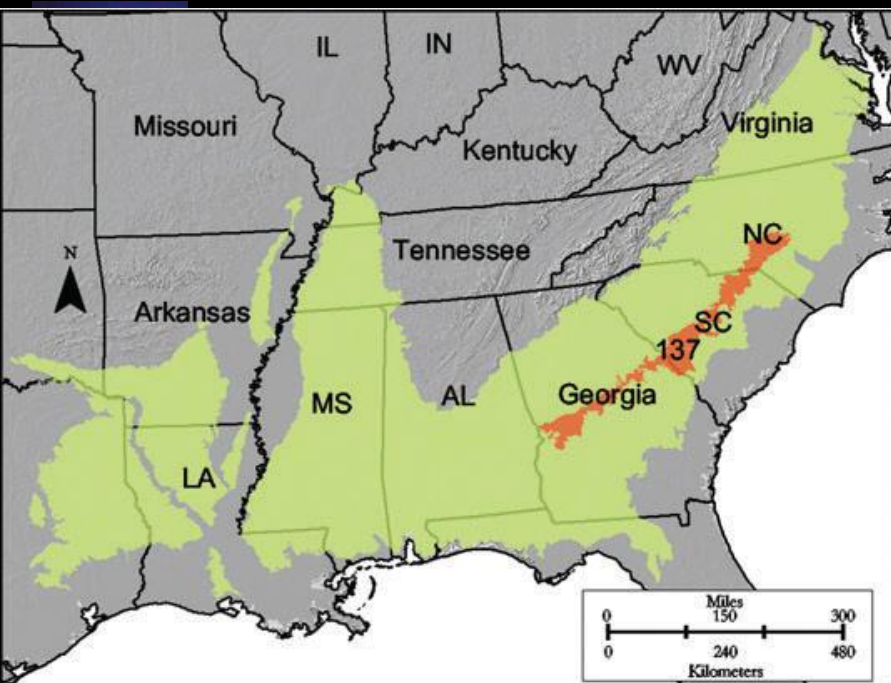
<http://www.sedlecky-kaolin.cz/en/kaolin-bentonit-kerastuk/>
consultado em novembro de 2016 (não está ativo em 2020)
<https://sedlecky-kaolin.cz/> (ativo em 2020)



Alemanha

AF4RWC
www.alamy.com

Kaolin china clay exploitation in Hirschau - Upper Palatinate - Bavaria - Germany



Georgia South Carolina - USA

The kaolin belt

Georgia's kaolin mining covers 13 counties extending along the "kaolin belt" from Americus to Augusta. The belt also extends into South Carolina, where some of the richest deposits are found.



Haile kaolinite mine, South Carolina



Georgia - USA

Washington County kaolinite mine





Angren - Uzbequistão



ANGREN KAOLIN



<http://angrenkaolin.uz/en/about-us>



Jari – Morro do Felipe (AP) – Brasil



Rheology

Our plant in Brazil offers the finest particle clay with the lowest rheology on the market. With higher solids, we save you money on the energy it takes to dry your paper coating. Less drying time means less energy output.

CADAM's clays also give a better overall fiber coverage and allow for much faster immobilization.



< <http://www.kaminllc.com/> >,
consultado em novembro de 2016

KaMin geologists locate the finest kaolin with the use of drilling surveys



KaMin

PERFORMANCE MINERALS

Kaolin Processing

Kaolin

Kaolin is crushed and fed into a blunger where it is dispersed in water to produce a clay slurry

Crusher

BLUNGER

CENTRIFUGE

Grit and other unwanted material is removed through the use of a centrifuge or dragboxes

DragBox

Underflow

Chemical Separation

Some KaMin operations use chemical separation to remove additional impurities

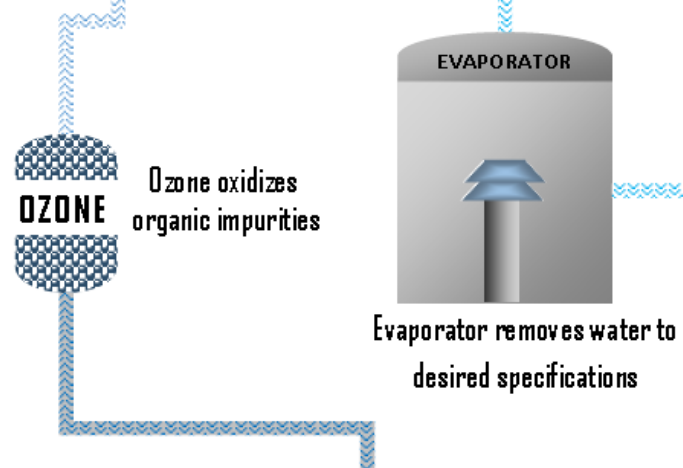
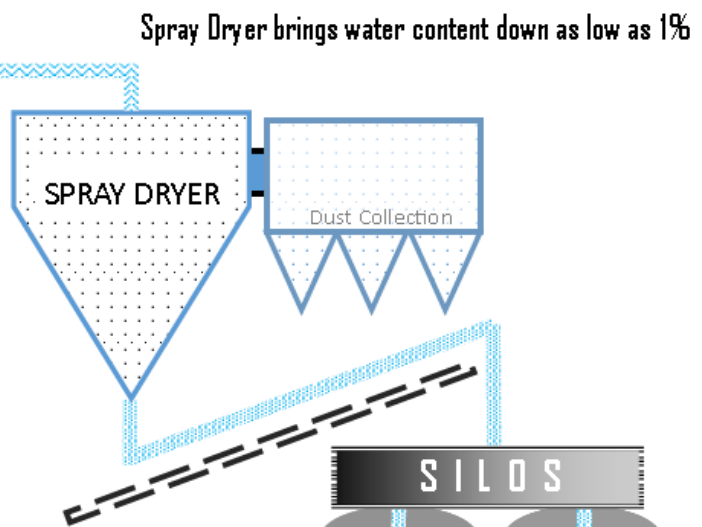
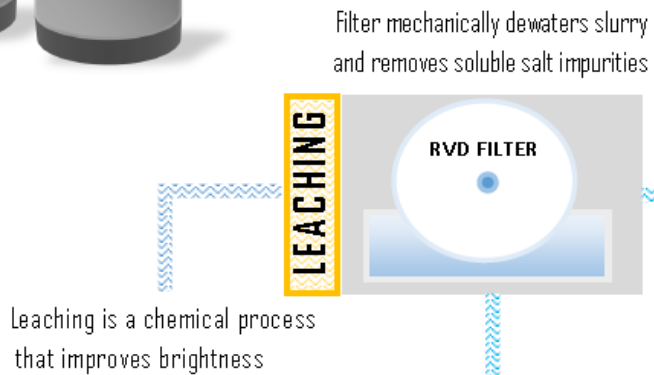
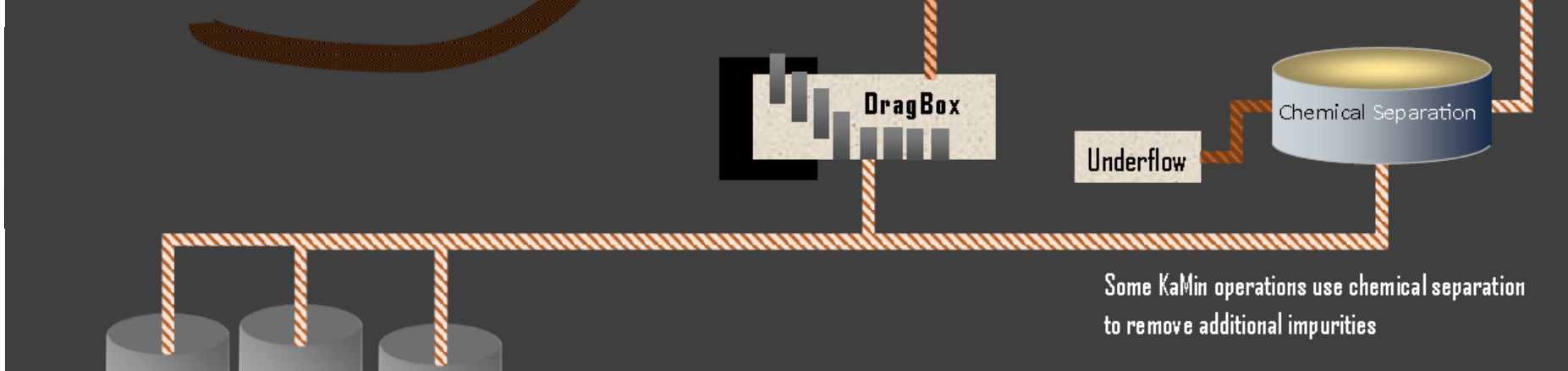
Plant

Storage

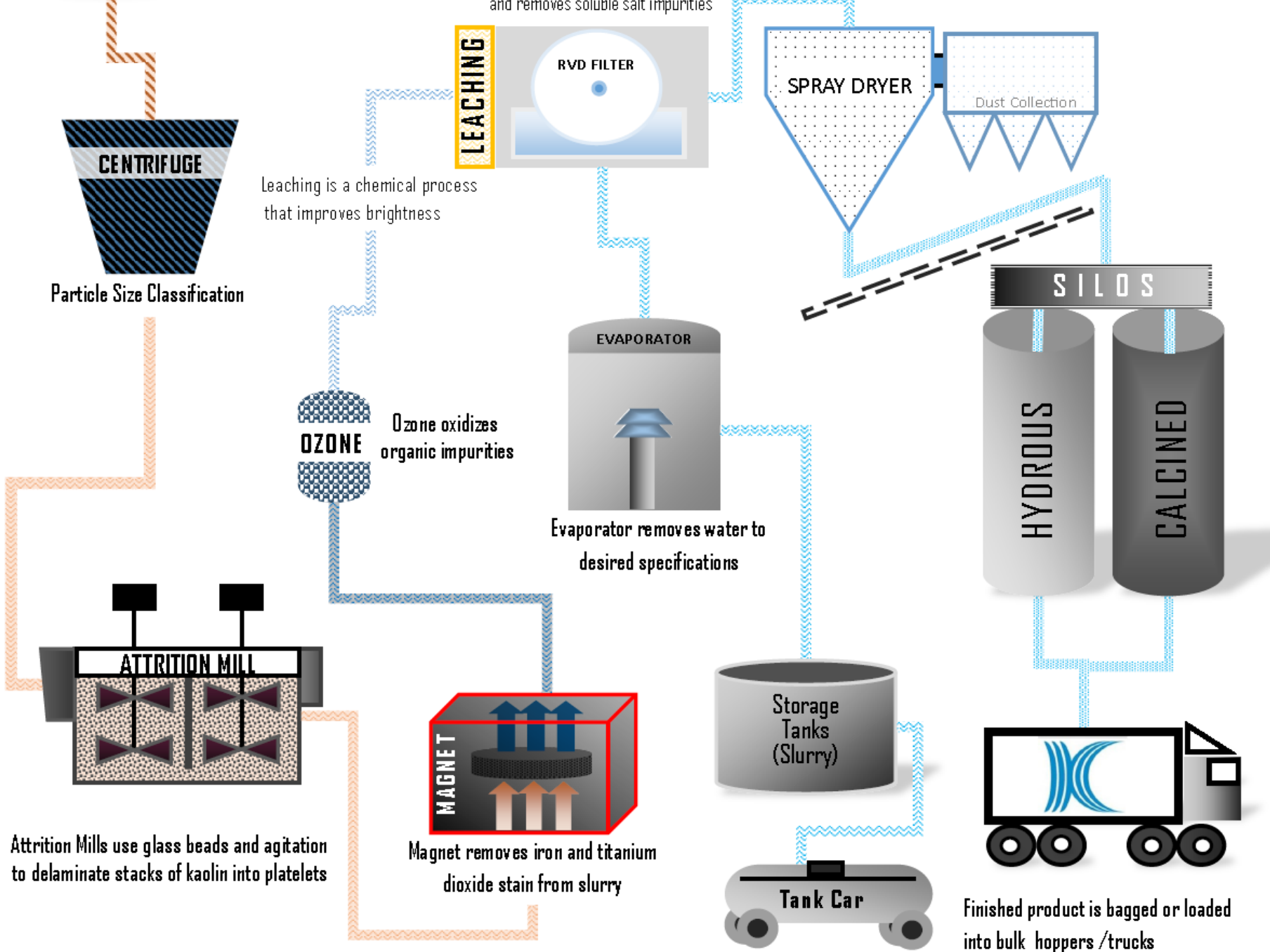
Tanks

Filter mechanically dewater slurry and removes soluble salt impurities

Spray Dryer brings water content down as low as 1%



and removes soluble salt impurities

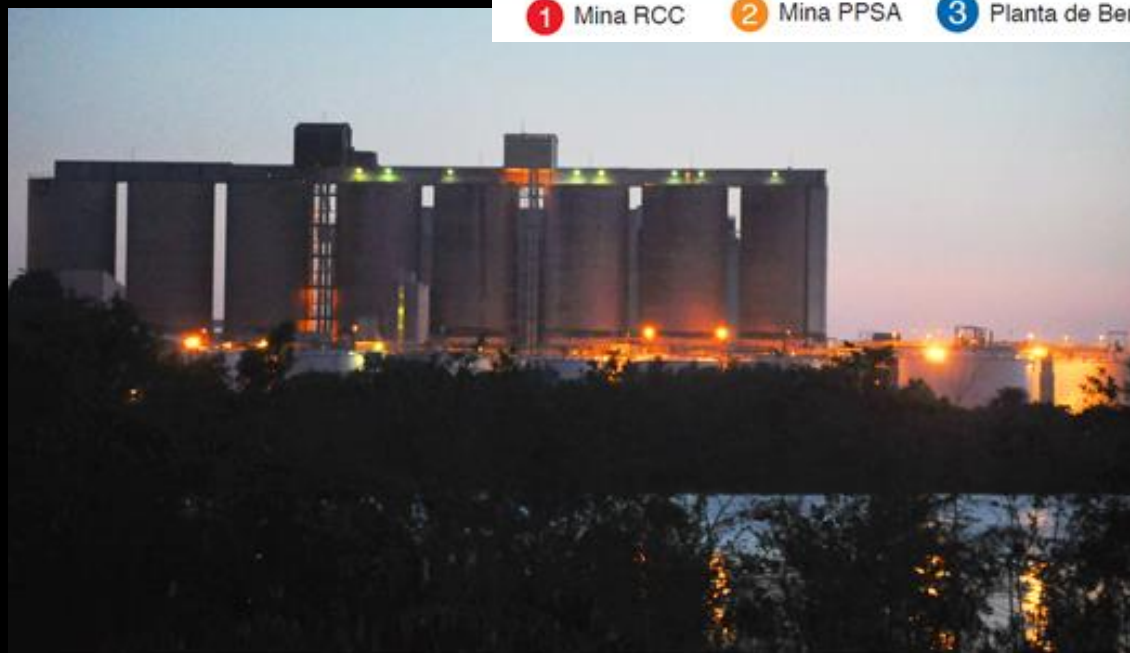


Vista da mina PPSA – Rio Capim - PA





Mina PPSA – Rio Capim - PA

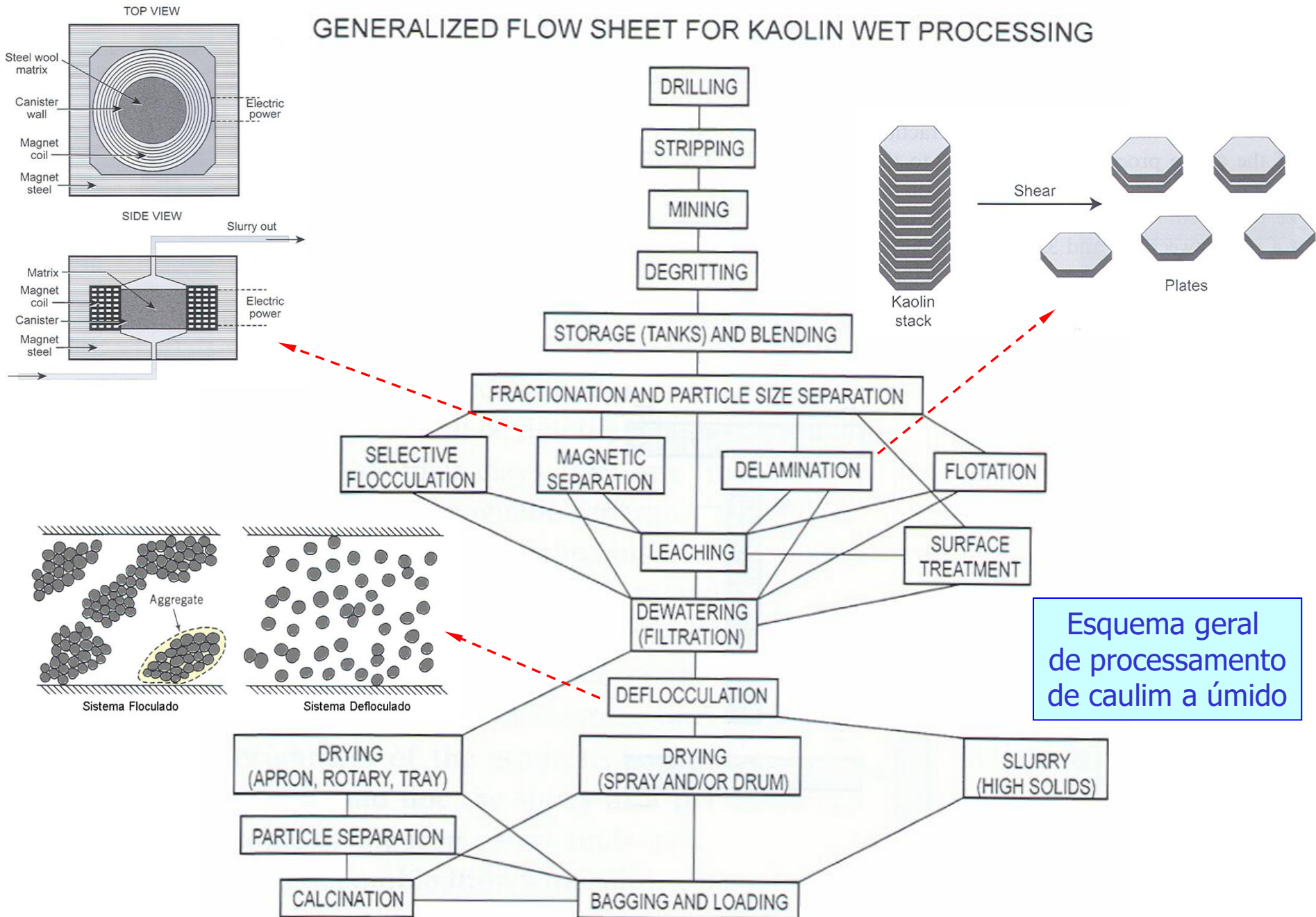


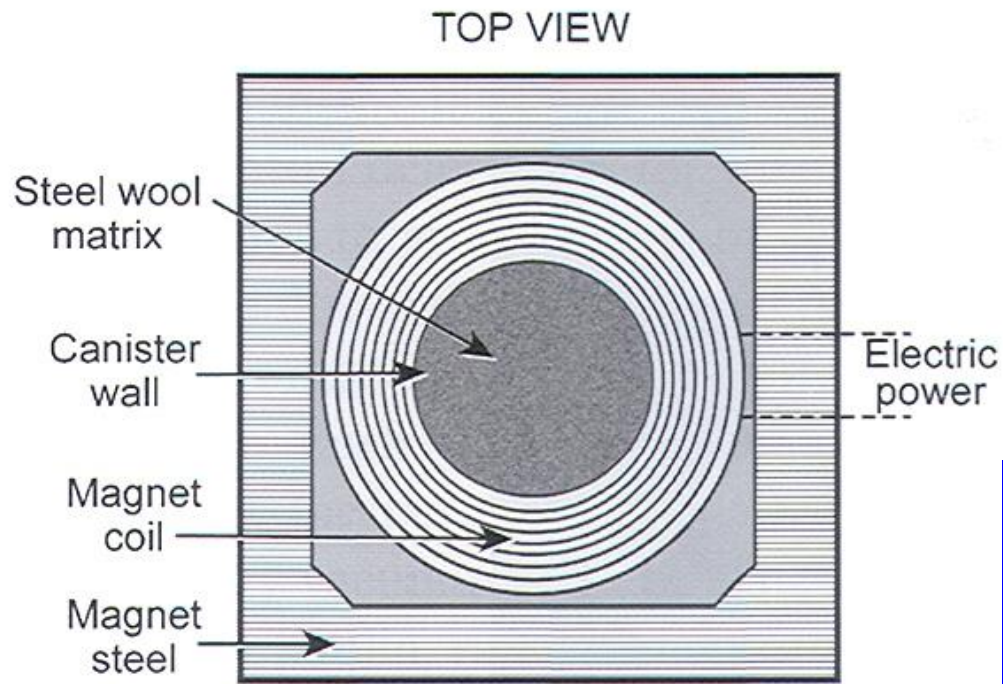


Vista aérea do porto da IRCC e PPSA Barcarena PA

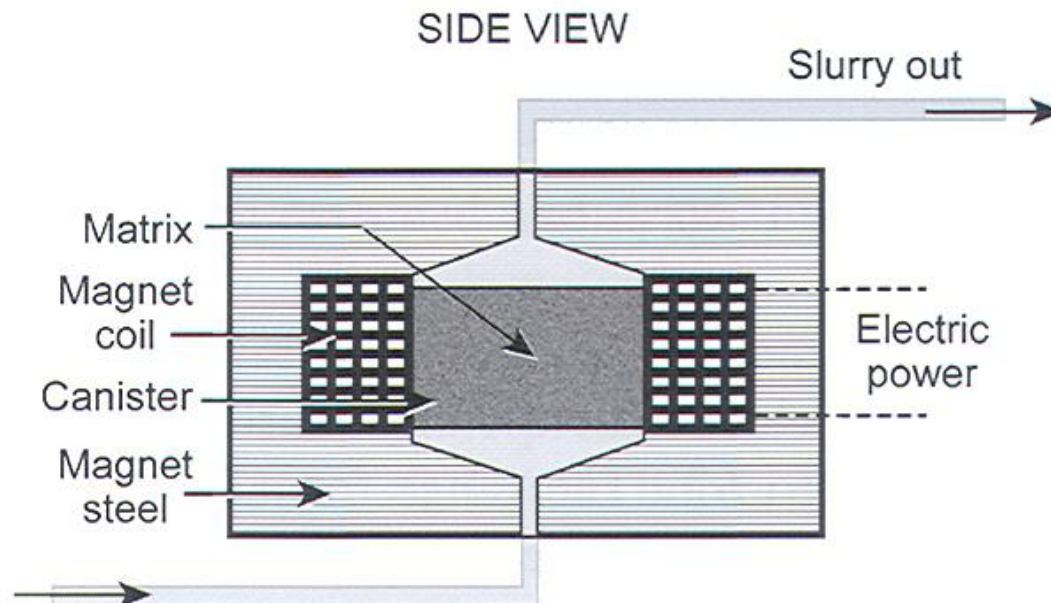


GENERALIZED FLOW SHEET FOR KAOLIN WET PROCESSING





Esquema do equipamento de separação magnética de compostos de ferro usado em caulim para papel





Kaolin (china clay) is one of many industrial minerals which require sophisticated, capital-intensive processing. Superconducting magnets are used to improve the whiteness of some kaolin from Cornwall by removing small quantities of iron-bearing minerals.





d. Os ensaios tecnológicos são facilitados quando existem especificações para os Caulins Industriais. Se não existirem, é necessário tomar produtos comerciais como referência, o que limita o valor dos resultados obtidos.

- No caso dos caulins para cobertura e para carga em papel, um exemplo de especificação (norte-americana) para propriedades físicas é dado a seguir [Prasad et al., *Applied Clay Science* **6**; 87-119 (1991)].

PROPRIEDADE	Caulim para Cobertura ("coating")	Caulim para Carga ("filler")
Porcentagem em peso de partículas com diâmetro equivalente (*) inferior a 10 μ m – Máximo de:	100%	85% - 97%
Porcentagem em peso de partículas com diâmetro equivalente (*) inferior a 2 μ m – Mínimo de:	89% - 92%	60% - 80%
Alvura (**) igual ou superior a :	90% - 92%	82% - 85%
Viscosidade a 71% em sólidos (***) inferior a :	74 cP	-----

(*) "diâmetro equivalente" por sedimentação por gravidade (Lei de Stokes); (**) Alvura ou Brancura (Brightness) $\neq$ Brilho ou Reflectância; (***) A concentração de 71% em sólidos é padronizada (é uma concentração crítica – pulo da η entre 69% e 71%)



→ **Products & Services**

→ **Kaolin**

→ **GCC**

→ **PCC**

→ **New Product Focus**

→ **Logistics**

→ **Quality**

→ **NPD**



As coatings, minerals are used in sophisticated formulations containing different pigments and chemical components to achieve high levels of brightness, gloss and print performance.

Coating Product Portfolio

Coating minerals are applied to the paper surface in a thin, even film to produce opaque, white, smooth and glossy paper with no increase in weight.

→ **Products & Services**

→ **Kaolin**

→ **GCC**

→ **PCC**

→ **New Product Focus**

→ **Logistics**

→ **Quality**

→ **NPD**



Fillers are added to the paper fiber at the beginning of the papermaking process, just prior to the formation of the paper web. Mineral fillers are designed to impart texture, opacity, whiteness and printability.

Filler Product Portfolio

Filler pigments have an increasingly important role in the success of uncoated woodfree, newsprint and supercalendered papers, as expectations in terms of print performance are constantly rising.

Um dos maiores produtores mundiais : IMERYS

*<http://www.imerys-paper.com/kaolin/kaolin.html>
(site consultado em 2018; não está vivo em 2020)*



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BASF's highly reactive metakaolin makes the bridges you drive stronger, more durable and resistant to chemical attack. The pozzolanic properties of MetaMax® are ideally suited for bridges, parking decks and other large structural projects where strength, durability and bright white concrete are important.

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Ansilex® 93

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Mattex® PRO

A specially engineered kaolin product for architectural paint applications with improved scrub resistance and burnish.

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MetaMax®

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Ensaio Tecnológicos

- O primeiro ensaio com objetivo de avaliação de um caulim é o de **análise granulométrica** - por sedimentação por ação da gravidade ou por dispersão de luz – para comparação com especificações para cobertura e/ou carga.
 1. É usado um defloculante-complexante do Ca: hexametáfosfato de Na; 5 mEq Na/100g da FA; a suspensão deve ser bem agitada, se possível com o auxílio de ultrassom, antes do ensaio de determinação da distribuição granulométrica.
 2. O método de medida pode ser gravimétrico (*Pipeta de Andreasen ou com o emprego de raios-X*) ou óptico (*com o emprego de laser*). Os métodos gravimétricos supõem que é válida a Lei de Stokes. Em todos os casos, calcula-se um diâmetro equivalente; importante lembrar que um cristal de caulinita é uma placa. Tem-se então as porcentagens em peso abaixo de $10\mu\text{m}$ e abaixo de $2\mu\text{m}$ (e também a porcentagem entre $44\mu\text{m}$ e $10\mu\text{m}$, por diferença de 100%, uma vez que a FA contém partículas inferiores a $44\mu\text{m}$).



3. É raríssimo encontrar valores para a % FA, em materiais naturais (sem beneficiamento), que sejam diretamente adequados para cobertura ou para carga para papel.
4. Contudo, consideremos os métodos de processamento industrial de argilas e estudemos um exemplo possível de ser observado.
 - i. Suponhamos que os resultados encontrados em uma análise granulométrica de uma **FA** (lembrar que FA $\rightarrow$ partículas $< 44\mu\text{m}$) correspondam a 72% de $\phi_{\text{equiv.}} < 10\mu\text{m}$ e 55% de $\phi_{\text{equiv.}} < 2\mu\text{m}$, valores obviamente fora das especificações.
 - ii. Lembrar que entre $44\mu\text{m}$ e $10\mu\text{m}$ existem $(100-72)=28\%$ de partículas; as partículas maiores que $10\mu\text{m}$ podem ser separadas, em laboratório ou industrialmente, por sedimentação por gravidade ou hidrociclone^(*).
 - iii. Supondo que todas as partículas de $\phi_{\text{equiv.}} > 10\mu\text{m}$ foram retiradas, a nova fração **FA₁** teria $[72/0,72] \% = 100\%$ de partículas de $\phi_{\text{equiv.}} < 10\mu\text{m}$, e $[55/0,72] \% = 73,3\%$ de partículas de $\phi_{\text{equiv.}} < 2\mu\text{m}$. Essa fração **FA₁** passaria na especificação de caulim para carga de papel.

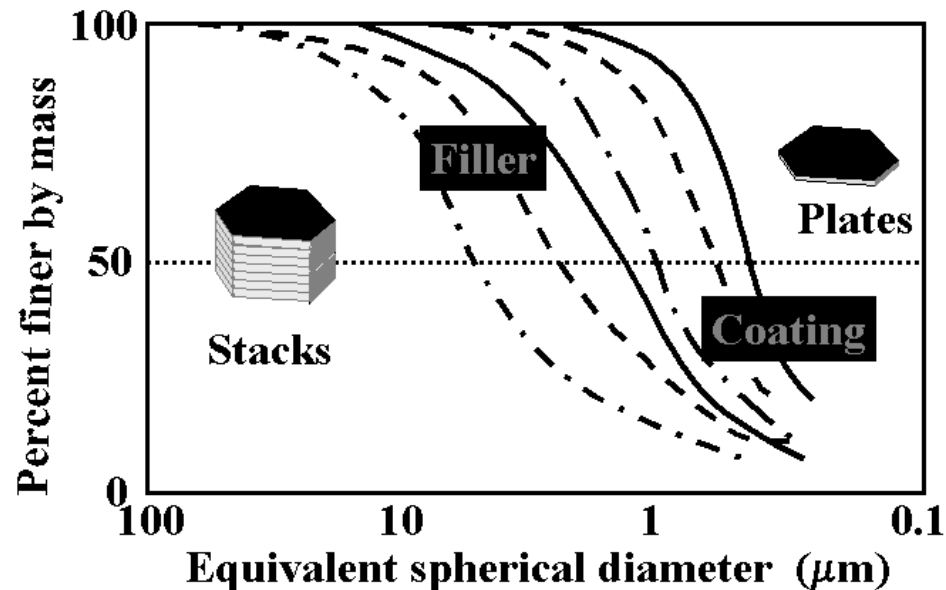
^(*) Hidrociclones

- Travinsky, H.; Eisenlohr, W. – *O Beneficiamento do Caulim*. Cerâmica **25**, 65; **26**, 122 (1980)
- Chaves, A.P. – *Teoria e Prática do Tratamento de Minérios*, vol.1, p. 185-189, Signus Editora, SP, 1996.



- iv. Utilizando sedimentação, hidrociclones ou centrifugação, é possível preparar uma outra fração **FA₂** na qual a porcentagem ponderal de partículas com $\phi_{\text{equiv.}} < 2\mu\text{m}$ seja maior do que 90%, o que colocaria a fração **FA₂** como passando o primeiro critério para cobertura de papel.
- v. Lembrar que o processo pode ser tecnicamente viável, porém para ser economicamente viável existe uma dependência de fatores externos aos ensaios em questão.

Kaolin Particle Size



Hagemeyer, *Pigments for Paper*, 1984, adapted

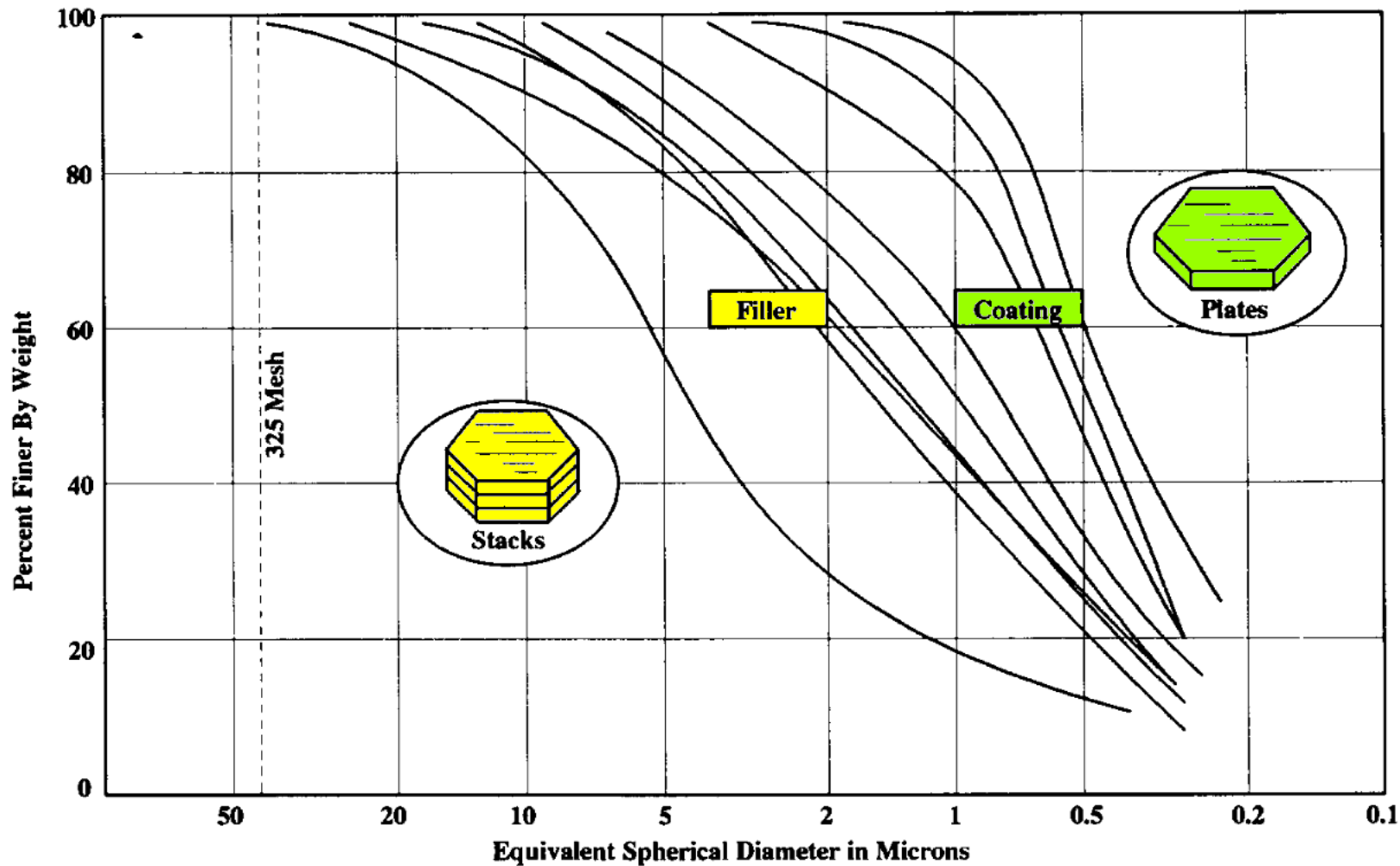


Fig. 9. Particle size distribution of coating and filler clays (Patterson and Murray, 1975).

[Prasad et al., *Applied Clay Science* **6**; 87-119 (1991)].

Aplicação : recobrimento de papel

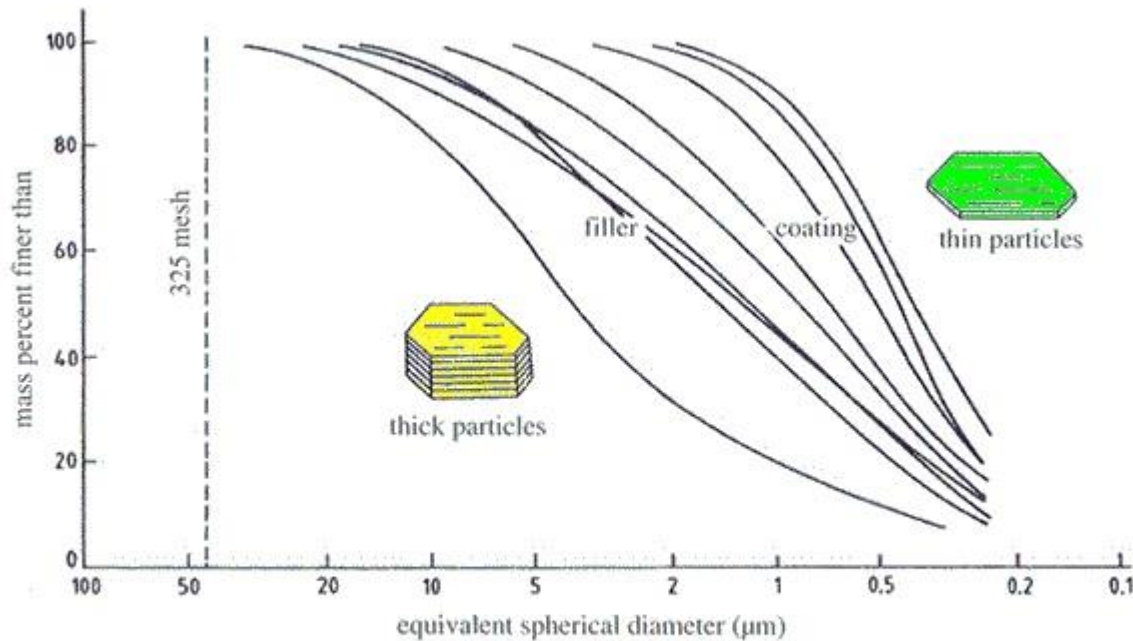
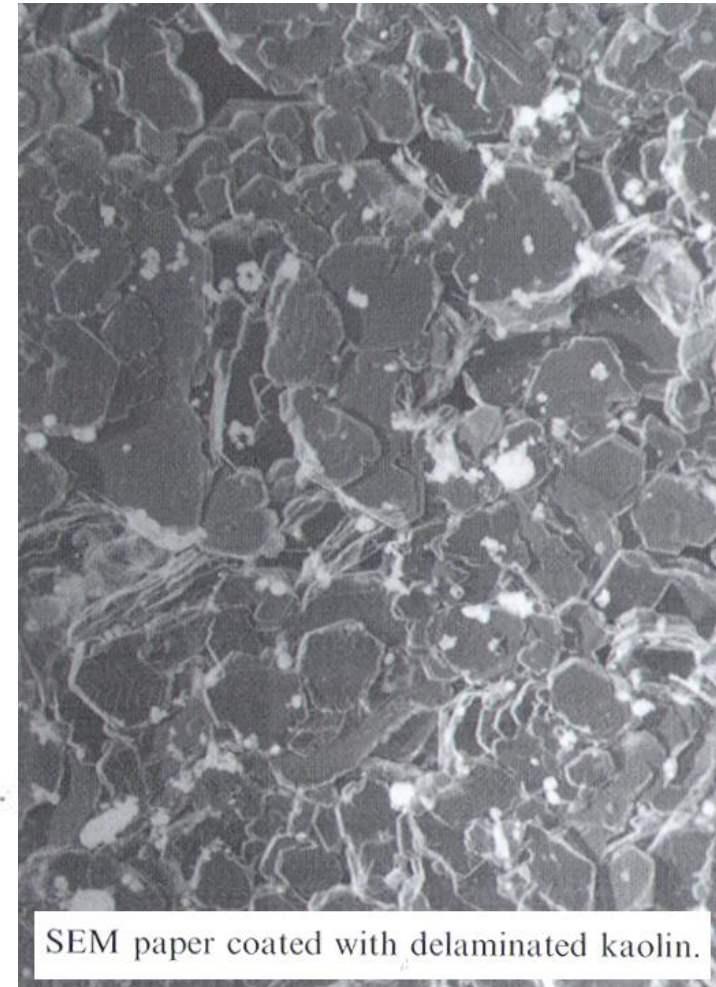


Fig. 10.1.1. Typical particle size distribution of filler and coating grade kaolins. Murray (1986).





- O ensaio seguinte com objetivo de avaliação da fração FA é o de **alvura**.
- 5. As frações **FA₁** (carga) e **FA₂** (cobertura) devem passar no critério "**Alvura**". Essa propriedade é medida em comparação com um padrão – um pó de óxido de magnésio – usando uma luz branca de comprimento de onda da ordem de 457 nm^(*) em equipamento padronizado. A luz refletida é tomada como 100% pelo fotômetro e calculada percentualmente para o caulim seco a 105°C/110°C e em pó. Para cobertura, a alvura deve ser igual ou superior a 90-92%, e para carga igual ou superior a 82-85%.

(*) norma TAPPI T-452 "Brightness of Pulp, Paper and Paperboard (Directional Reflectance at 457 nm)"



6. Também esses mínimos são muito raramente atingidos pelas frações **FA₁** e **FA₂**. A causa é a seguinte: caulinita é branca; logo, sua alvura é 100%. Contudo, o caulim, naturalmente, contém minerais acessórios, de diferentes composições químicas, teores e granulometrias. Alguns desses minerais acessórios podem existir nas duas frações: minerais de ferro e titânio.
- O **ferro** pode estar presente na forma de óxido [hematita Fe_2O_3] e de hidróxidos de Fe^{3+} [$\text{Fe}(\text{OH})_3$ e $\text{FeO}(\text{OH})$]; todos são compostos externos aos cristais de caulinita, e o ferro pode ser reduzido a Fe^{2+} , que por sua vez pode ser solubilizado, complexado e extraído → dessa forma, a alvura melhora, conforme diminua o teor de ferro do caulim.
 - Ferro, como mineral de ferro e externo aos cristais de caulinita, pode ser retirado também por “**filtração magnética**”, com o emprego de campo magnético de altíssima intensidade, com a conseqüente melhoria da alvura das frações **FA₁** e **FA₂**. Infelizmente, Fe^{3+} em substituição isomórfica do Al^{3+} não pode ser removido; nesse caso, não é possível melhorar a alvura.
 - O **titânio** ocorre como TiO_2 , em várias formas de minerais, todas de coloração cinza, baixando a alvura. Caulins sedimentares costumam ter maiores teores de TiO_2 do que caulins residuais.
 - A forma de retirar os minerais de titânio é por flotação seletiva.



Análises Químicas de Caulins

Caulins norte-americano (sedimentar), inglês (residual, hidrotérmico) e brasileiros (sedimentares) mostrando as diferenças em teores de ferro e titânio

Óxido	Caulim da Geórgia	Caulim da Inglaterra	Caulim do Jari	Caulim do Capim	Caulim de Manaus	Caulinita Teórico
SiO ₂	45,30	46,77	46,0	46,0	45,6	46,9
Al ₂ O ₃	38,38	37,79	37,0	39,0	38,4	39,3
Fe ₂ O ₃	0,30	0,36	1,8	0,62	0,91	-----
TiO ₂	1,44	0,02	1,0	0,77	0,57	-----
MgO	0,25	0,24	0,03	0,01	0,13	-----
CaO	0,05	0,13	0,06	0,01	< 0,05	-----
Na ₂ O	0,27	0,05	0,10	0,19	0,08	-----
K ₂ O	0,04	1,49	< 0,05	< 0,05	< 0,05	-----
P.F. (950°C)	13,97	12,97	14,0	13,9	14,3	13,8

TABLE 2. Comparison of kaolin qualities from three Amazon deposits.

Deposit	Jari River	Capim	Manaus
Name of mine	Felipe II	Ipixuna	Prospect
Company,	CADAM – Caemi,	PPSA – Caemi,	Min. Horboy Clays
Product name	Amazon Plus	Century	–
Capacity (Kt) 2005	900	600	No production
Sales (Kt) 2005	720	522	No sales
Reserves (Mt)	100	50	100
Type of deposit	Sedimentary	Sedimentary	Sedimentary
Geology	Lateritic profile	Kaolin lenses	Kaolinitic sand
Morphology	Pseudo-hexagonal	Pseudo-hexagonal	Pseudo-hexagonal
Product/Test result	Amazon Plus	Century	Coating clay
ISO brightness	87.5	88.8	89.0
ISO yellowness	5.2	4.7	5.3
Particle-size distribution (wt.%)			
>10 µm	0.1	0.02	0.01
<2 µm	98	81	94
<1 µm	95	61	84
<0.5 µm	80	33	59
<0.25 µm	46	10	14
<0.1 µm	10	–	–
Surface area	15	11	12
Viscosity concentration (%)*	74	73	75
Aspect ratio	9	14	–
Chemistry (wt.%)			
SiO ₂	46.0	46.0	45.6
Al ₂ O ₃	37.0	39.0	38.4
Fe ₂ O ₃	1.8	0.62	0.91
TiO ₂	1.0	0.77	0.57
CaO	0.06	0.01	<0.05
MgO	0.03	0.01	0.13
K ₂ O	<0.05	<0.05	<0.05
Na ₂ O	0.10	0.19	0.08
LOI	14.0	13.9	14.3
Mineralogy (wt.%)			
Kaolinite	100	100	100
Mica	–	–	–
Anatase/rutile	trace	–	–

* Viscosity concentration measured at 5 poise at 22°C using a Brookfield Viscometer at 100 rpm.

Clay Minerals (2006) **41**, 697–716

Kaolin and halloysite deposits of Brazil

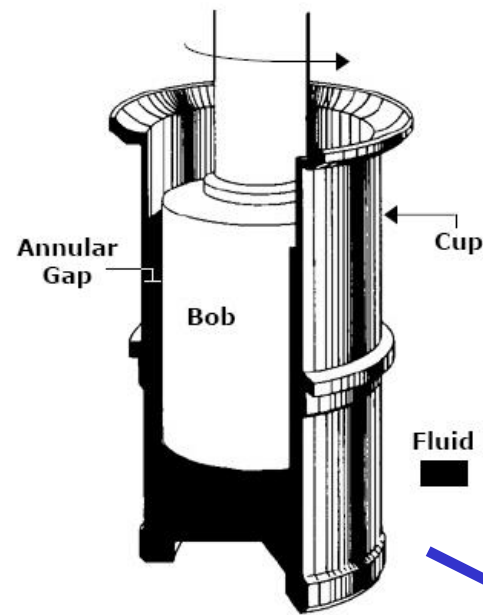
I. R. WILSON^{1,*}, H. DE SOUZA SANTOS² AND P. DE SOUZA SANTOS³



- O ensaio seguinte com objetivo de avaliação das propriedades tecnológicas é o de **viscosidade**.
- 7. Admitamos que as frações **FA₁** e **FA₂** tenham passado pelo critério “Alvura”, após terem sido extraídos os compostos de Fe e Ti. O terceiro ensaio tecnológico é o de **viscosidade a 71% de sólidos**.
 - As viscosidades são medidas em dispersões aquosas defloculadas segundo o método TAPPI T-648 (método padronizado para as indústrias de papel).
 - As viscosidades sob tensões baixas de cisalhamento são medidas em um viscosímetro Brookfield a 20 rpm. As viscosidades sob tensões elevadas de cisalhamento são medidas em um viscosímetro Hercules com velocidades de 700 rpm a 1100 rpm.
 - Uma boa barbotina ou tinta para cobertura de papel para ser bombeada deve ter viscosidade baixa sob tensão de cisalhamento elevada.
 - A Tabela a seguir mostra, para caulim da Geórgia, EUA, as viscosidades sob tensões de cisalhamento baixas e elevadas.



Viscosímetro Brookfield
(baixa tensão de cisalhamento)



Viscosímetro Hercules
(alta tensão de cisalhamento)



Viscosidades sob tensões de cisalhamento baixas e elevadas para um caulim da Geórgia

Amostra	% $\phi < 2\mu\text{m}$	Visc. T.Ciz. BAIXA	Visc. T.Ciz. ALTA	% sólidos
1	95	5,60 poises	0,62 poises	71
2	92	4,40 poises	1,15 poises	71
3	83	4,00 poises	1,81 poises	71

Ref.: Prasad, M.S.; Reid, K.J.; Murray, H.H. et al., Appl. Clay Sci. 6, 87-119 (1991); Bundy, W.M.; Ishley, J.N., Appl. Clay Sci. 5, 397-420 (1991)

- A amostra 1 é a melhor para cobertura de papel e esse fato parece estar correlacionado diretamente com o maior teor de partículas com diâmetro equivalente menor do que $2\mu\text{m}$, o qual foi, provavelmente, conseguido por processamento industrial.

8. Neste ponto, admitamos que ambas frações **FA₁** e **FA₂** tenham sido aprovadas nas propriedades físicas, isto é, em granulometria, alvura e viscosidade. A próxima etapa seria o teste em **ensaios de fabricação de papel**. Contudo, especialmente no Brasil, é recomendável que seja feita microscopia eletrônica de transmissão de **FA₂** para verificar se os cristais de caulinita são hexágonos e se haloisita tubular está ausente; interessante também verificar por DRX se a caulinita é “bem cristalizada” (“low defect”).



Engineered clay products for the paper industry

Haydn H. Murray^{a,*}, Jessica Elzea Kogel^b

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^bThiele Kaolin Co., Sandersville, GA 31082, USA

Table 1
Particle size and brightness of regular coating clays

Regular coating clay	Particle size	Brightness
No. 3	70–72% < 2 μ	84.5–86
No. 2	80–82% < 2 μ	85.5–87
No. 1	90–92% < 2 μ	87–88

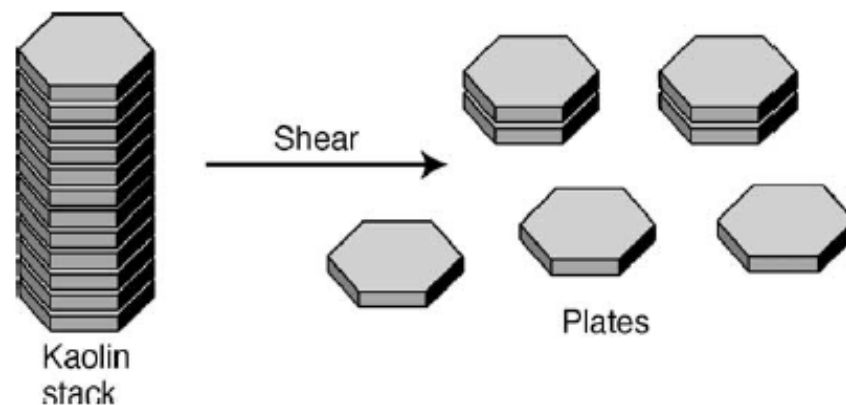


Fig. 1. Delamination of kaolin stacks.

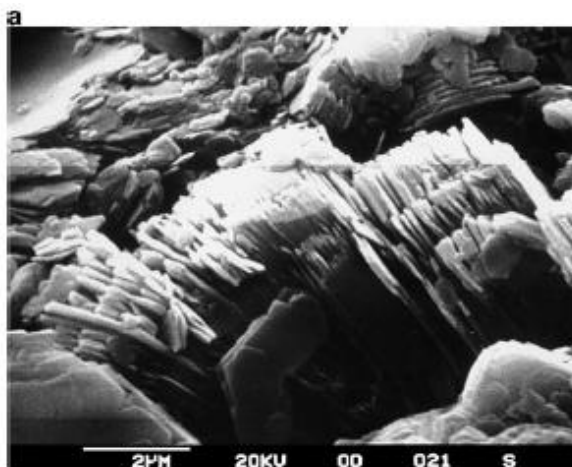


Fig. 2. (a) SEM of large kaolin stacks. (b) SEM of delaminated stack plates.

Runnability is the ease of applying thin coatings at high speed and high solids content without streaks, scratches, skips, or paper breakage. Dilatancy generally correlates with poor runnability. Particle size and particle size distribution can be controlled to some extent to produce coating clays that are newtonian or nearly so in their flow characteristics at high rates of shear. Fig. 3 shows the relationship between thixotropic, newtonian, and dilatant flow with increasing rates of shear. A coating kaolin with good runnability can be achieved when an optimal percentage of fine particles are present which promotes more efficient particle packing (Fig. 4). Thus, a kaolin coating clay can be engineered to have good runnability.

Ultra fine particles in kaolin, however, do not effectively scatter light because the wave length of light is nearly the same as these very fine particles. Therefore, both opacity and brightness are affected as is binder demand because of the increased surface areas of the ultra fine particles. Brightness and opacity are functions of particle size and particle packing, adhesive content, and the amount of voids. Thus, by removing a significant portion of the ultrafine particles in the size range of 0.5 μ m and smaller, the light scatter is enhanced which increases the brightness and opacity.

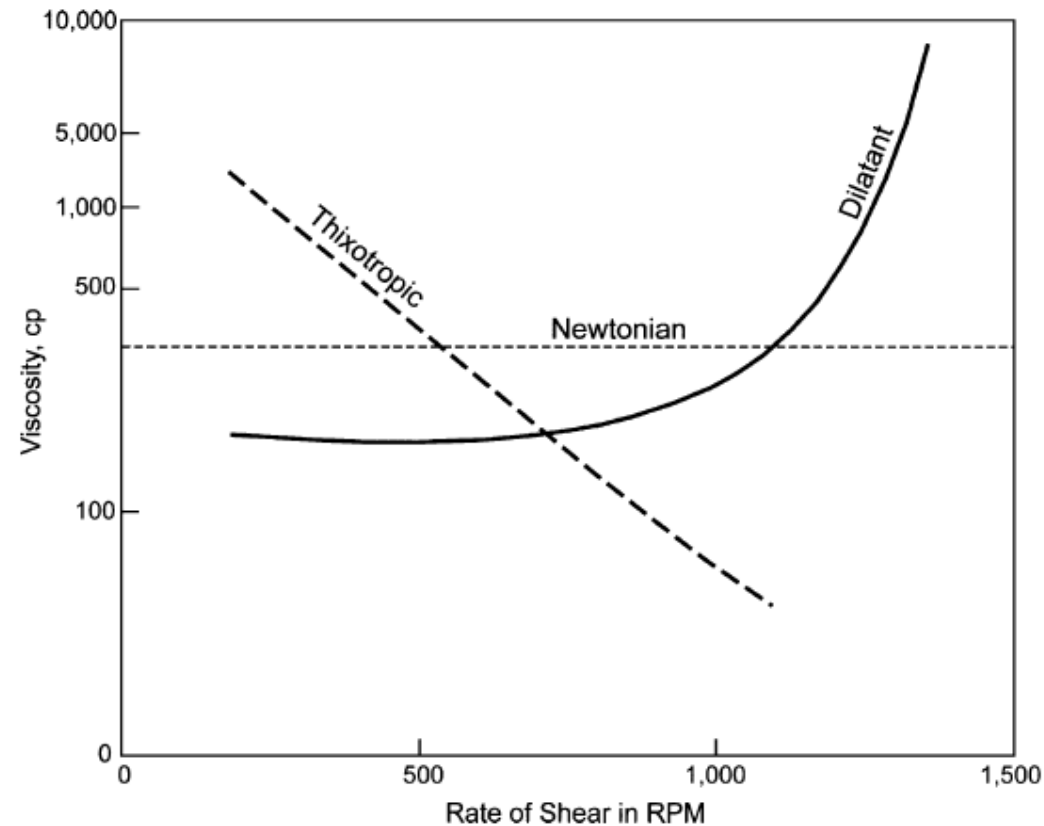


Fig. 3. Relationship between viscosity and rate of shear.

Particle Packing in Kaolinite-Water Systems

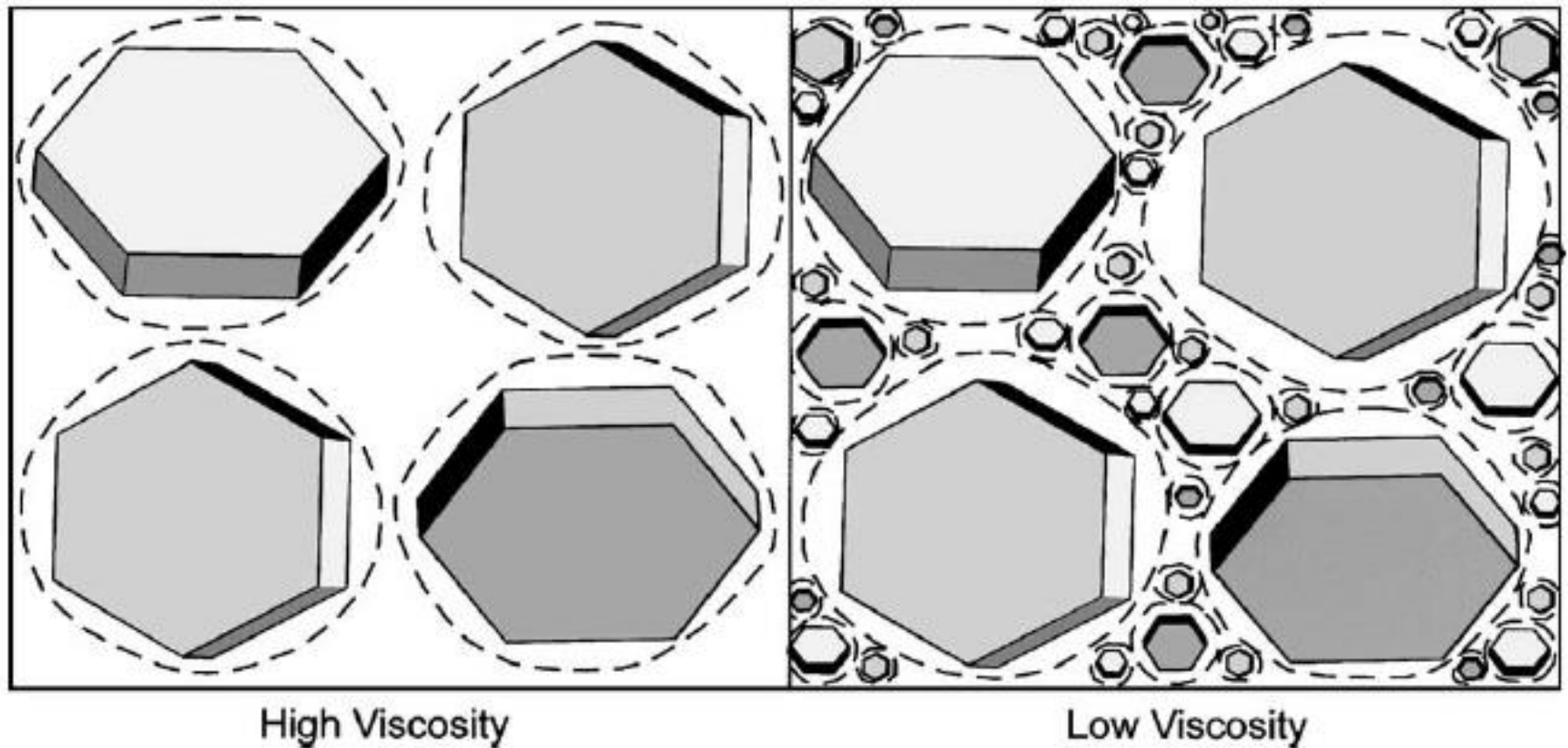


Fig. 4. Schematic representation of the relationship of viscosity to particle packing.

Runnability is the ease of applying thin coatings at high speed and high solids content without streaks, scratches, skips, or paper breakage. Dilatancy generally correlates with poor runnability. Particle size and particle size distribution can be controlled to some extent to produce coating clays that are newtonian or nearly so in their flow characteristics at high rates of shear. Fig. 3 shows the relationship between thixotropic, newtonian, and dilatant flow with increasing rates of shear. A coating kaolin with good runnability can be achieved when an optimal percentage of fine particles are present which promotes more efficient particle packing (Fig. 4). Thus, a kaolin coating clay can be engineered to have good runnability.

Ultra fine particles in kaolin, however, do not effectively scatter light because the wave length of light is nearly the same as these very fine particles. Therefore, both opacity and brightness are affected as is binder demand because of the increased surface areas of the ultra fine particles. Brightness and opacity are functions of particle size and particle packing, adhesive content, and the amount of voids. Thus, by removing a significant portion of the ultrafine particles in the size range of 0.5 μ m and smaller, the light scatter is enhanced which increases the brightness and opacity.

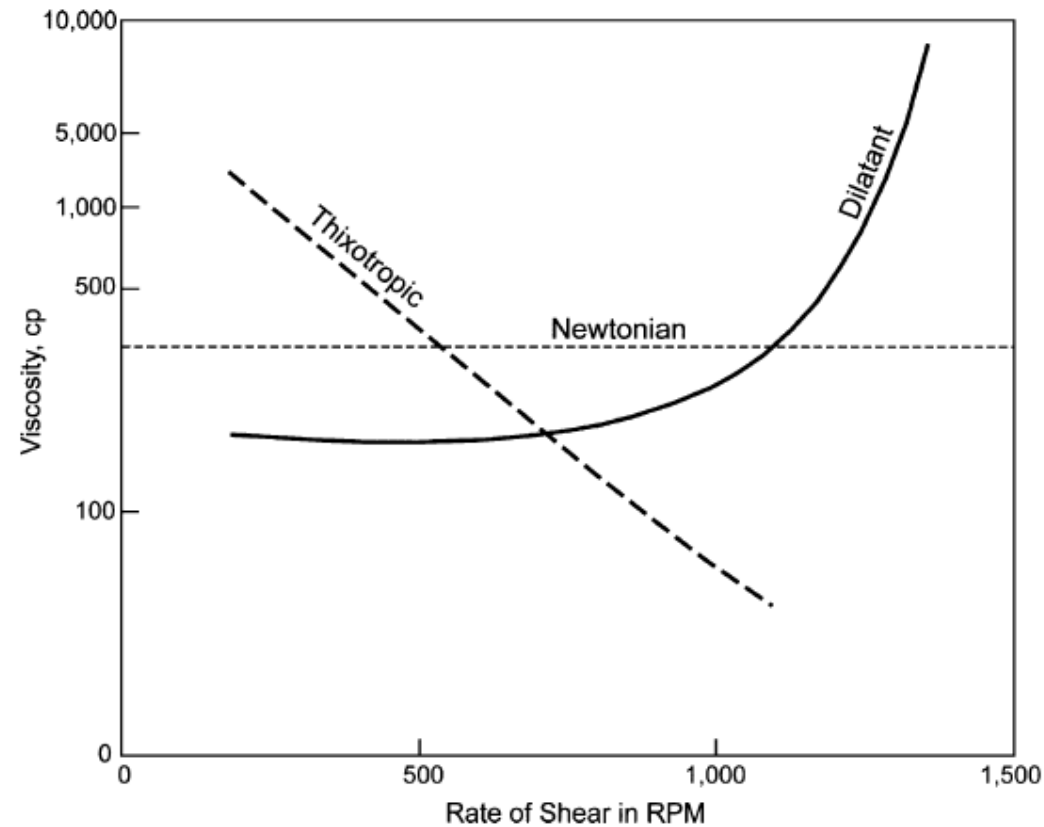
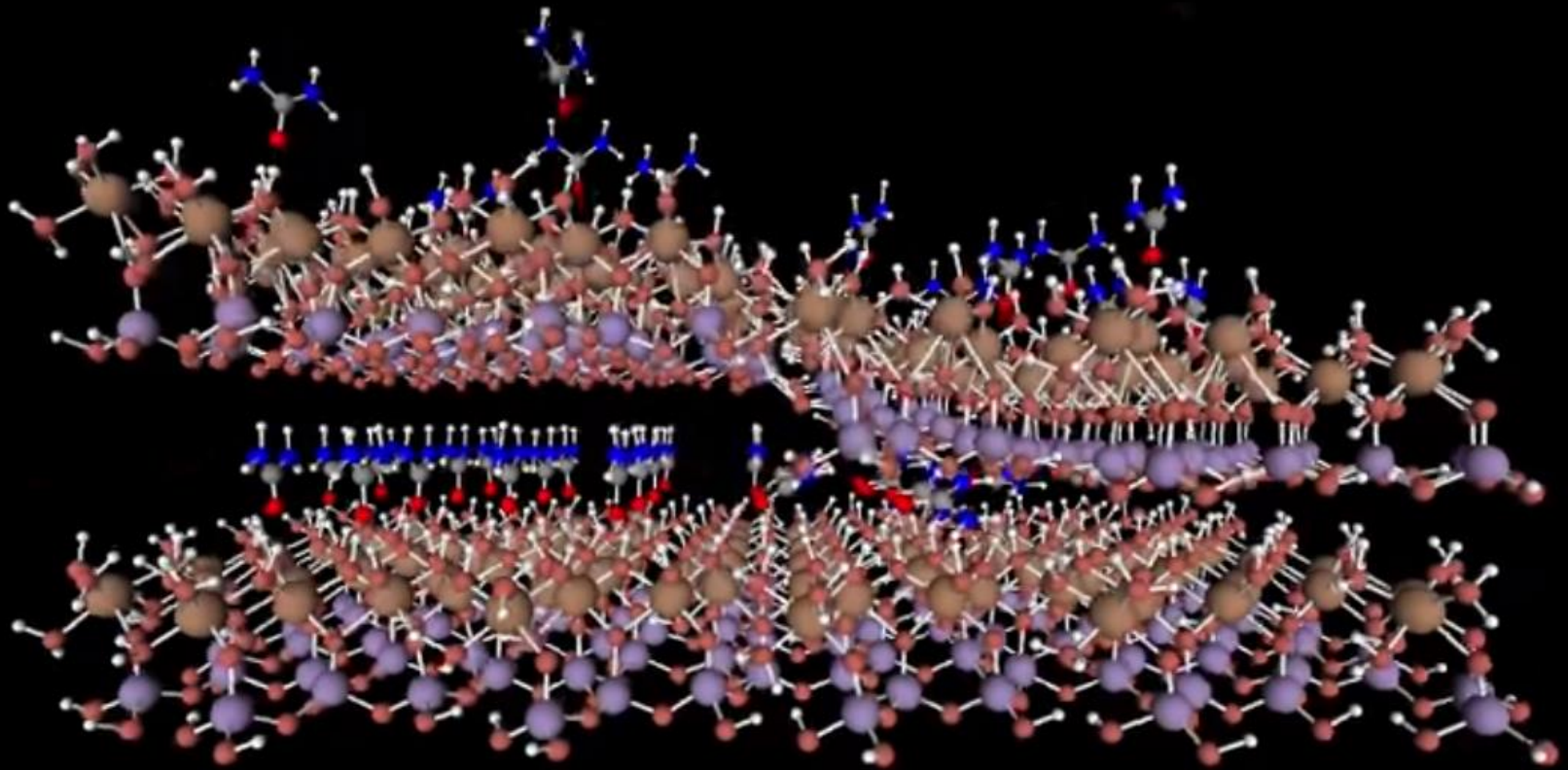


Fig. 3. Relationship between viscosity and rate of shear.



Intercalação de Caulinita



Animação muito boa ■ Urea intercalation of kaolinite (a stepwise process)
<https://www.youtube.com/watch?v=xBTiA9viIQo>



Mecanismo de Intercalação de Caulinita

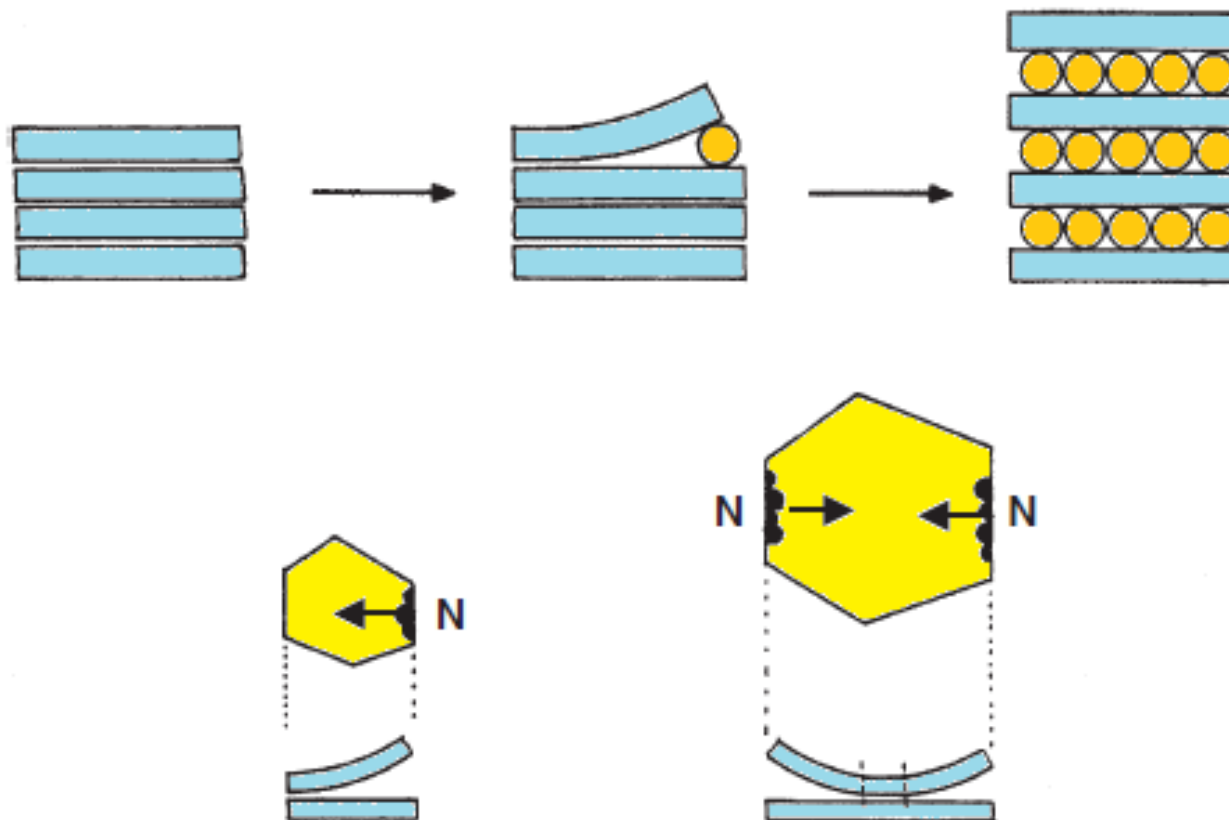


Fig. 7.3.3. Mechanism of intercalation. N nucleation sites, arrow: moving reaction front.

Bergaya, F.; Theng, B.K.G.; Lagaly, G. (eds.). *Handbook of Clay Science*. 2ª Ed.
Developments in Clay Science 5. Elsevier. Vol. 1, cap. 7.3 (2006).

Table 7.3.1. Reaction conditions and basal spacing of a few kaolinite intercalation compounds

Guest compound	Basal spacing (nm)	Reaction conditions
None	0.71	
Formamide	1.01	4 days, 60 °C
Hydrazine hydrate	1.04	1 day, 60 °C
Urea*	1.07	8 days, 60–110 °C
<i>N</i> -methylformamide	1.08	2 days, 60 °C
Dimethyl sulphoxide	1.12	30 h, 50 °C
	1.12	20 min, 150 °C*
Potassium acetate*	1.40	1 day, 65 °C, pH = 8
Ammonium acetate*	1.41	20 days, 20 °C, pH = 8–9

From Weiss et al. (1966); Weiss and Orth (1973); Vempati et al. (1996)

*In saturated aqueous solutions.

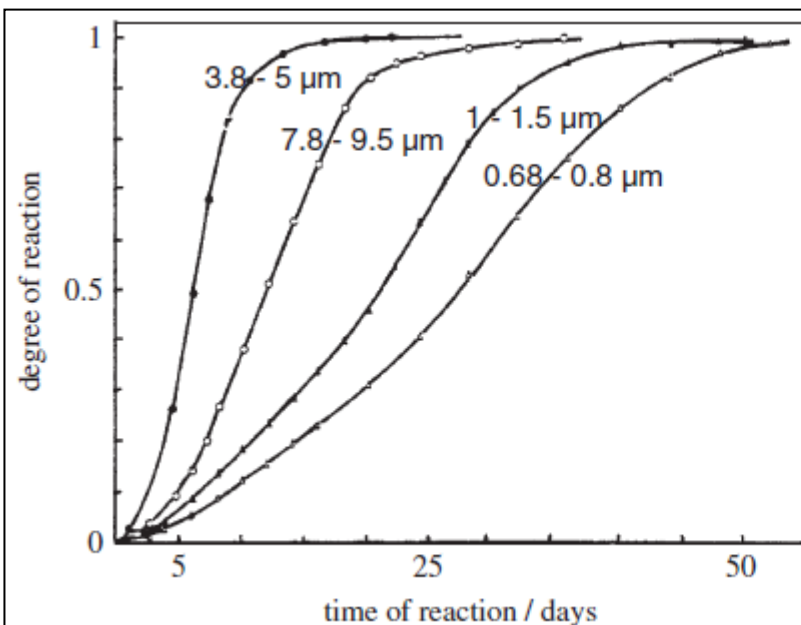
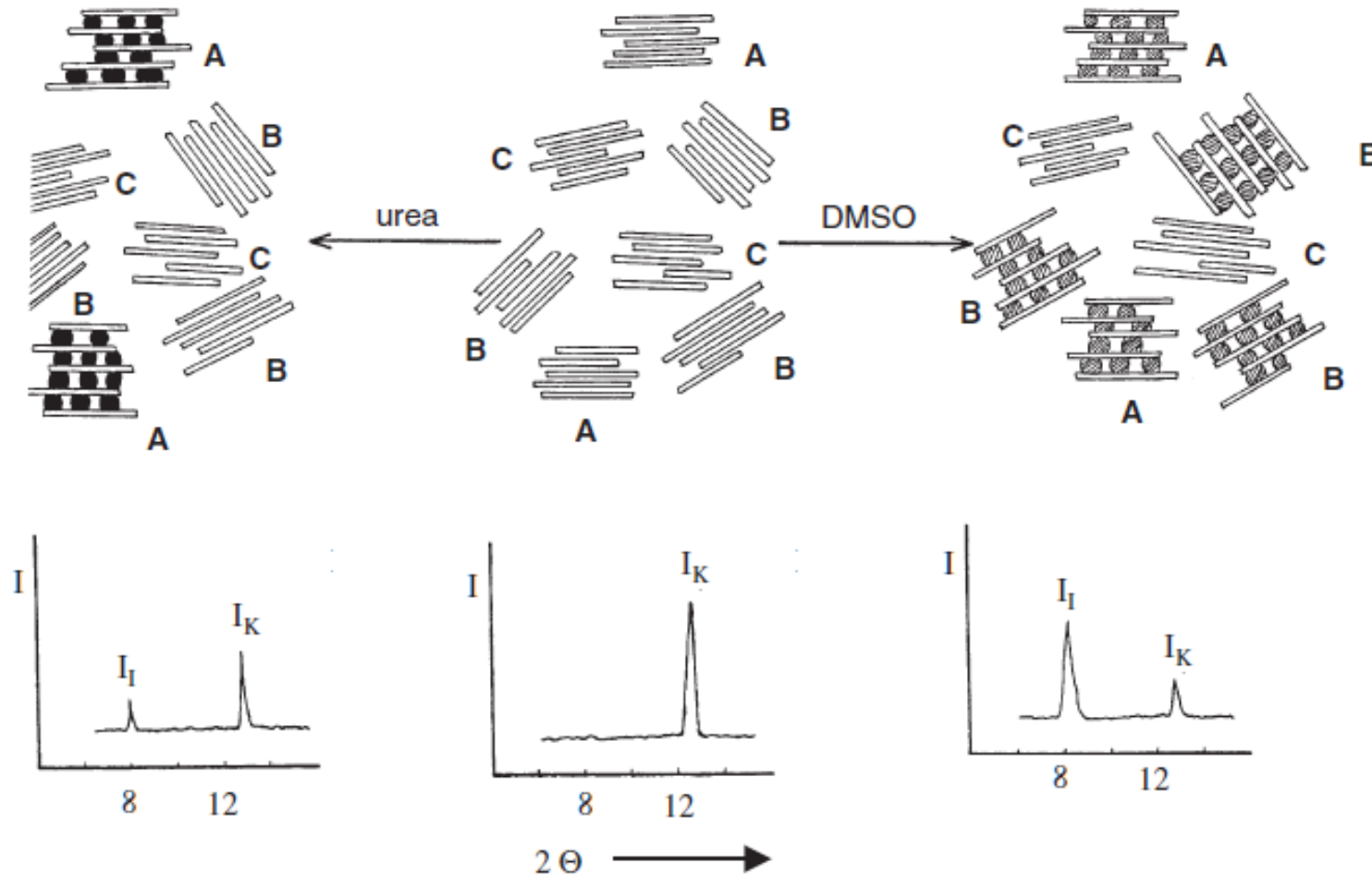


Fig. 7.3.2. Intercalation of urea (saturated aqueous solution at 65 °C) into kaolinites of different particle sizes (Weiss et al., 1970).



Tipos de Caulim – Intercalação



TIPO A

Tipo mais reativo

Intercala diretamente com DMSO, ureia e com outras espécies químicas

TIPO B

Intercala com DMSO mas não com ureia

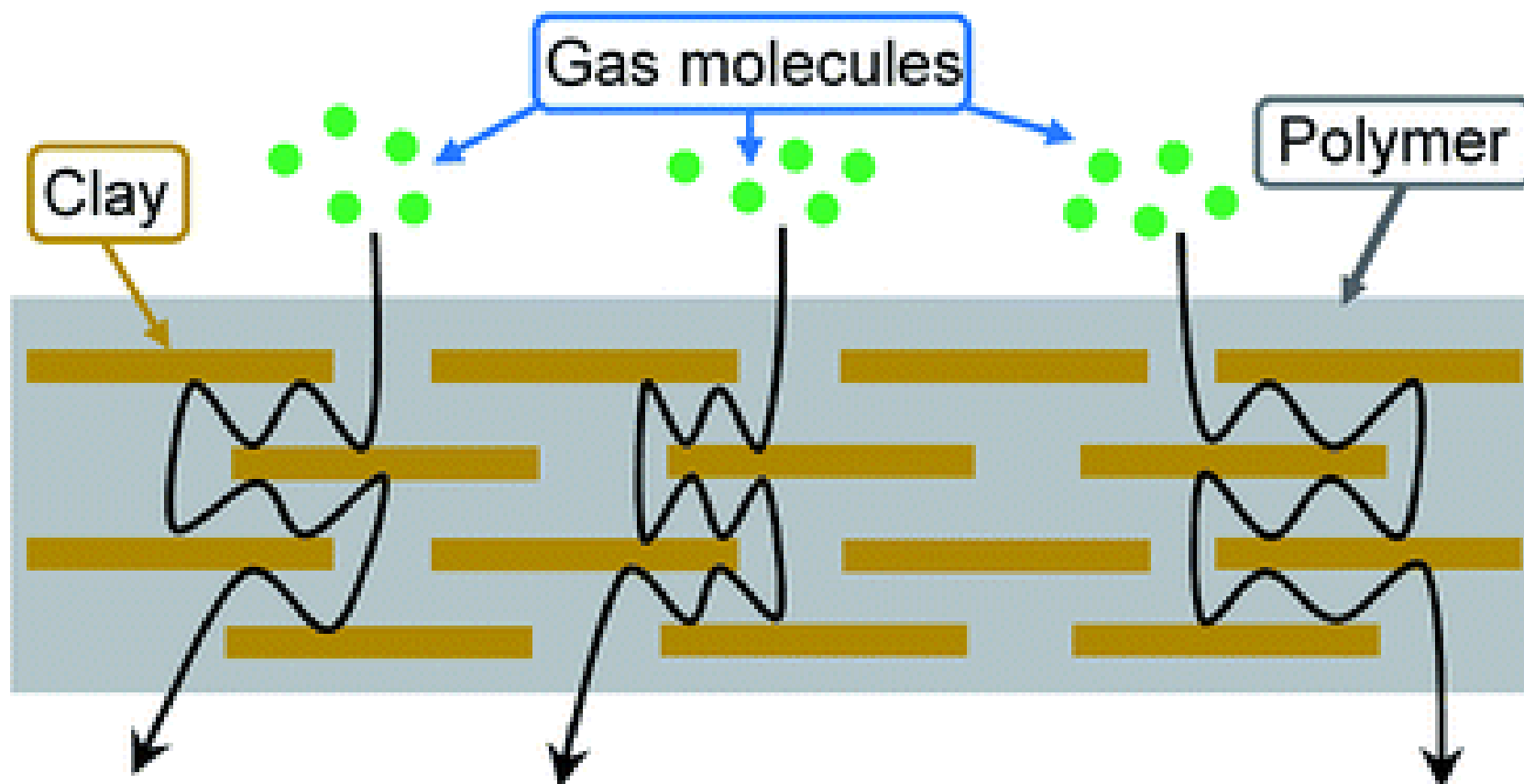
TIPO C

Não-reactivo (não intercala)

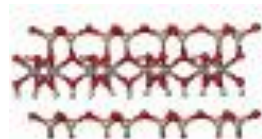
Fig. 7.3.4. Reaction of a kaolin sample consisting of three types of kaolinites (reaction types A, B, and C) with dimethyl sulphoxide (DMSO) and urea (see text). Fernandez-Gonzales et al. (1976).



Exemplo de Aplicação – Barreira a Gases

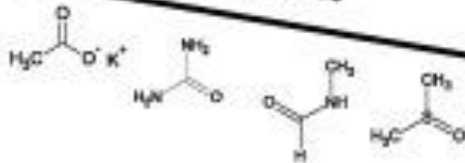


Intercalação em Caulinita



Kaolinite

One step intercalation of selected compounds



Intercalated/Delaminated/exfoliated nanocomposites

Pre-intercalate

Intercalated compounds

Grafted compounds



Grafted ionic liquid



Grafted neutral compound

- Nanocomposites
- Adsorbents
- Electrochemical sensors
- Catalyst support
- Solid ionic conductors

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journal homepage: www.elsevier.com/locate/clay



Research paper

Functional nanohybrid materials derived from kaolinite

Gustave Kenne Dedzo ^{a,b}, Christian Detellier ^{a,*}



BALL CLAYS





“Ball Clays” = Argilas Plásticas para Cerâmica Branca

- *Ball clay is an extremely rare mineral resource found in very few places around the world. Its name dates back to the early methods of mining when specialized hand tools were used to extract the clay in rough cube shapes of about 30 cm. As the corners were knocked through handling and storage these cubes became rounded and 'ball' shaped. It also is sometimes referred to as plastic clay.*
- *Ball clays are sedimentary in origin. Ancient rivers and streams washed kaolinite (formed from decomposed granite) from its parent rock. As the streams flowed from upland areas the mixed with other clay minerals, sands, gravels and vegetation before settling in low-lying basins to form overlaying seams of ball clay. Ball clays usually contain three dominant minerals: from 20-80% kaolinite, 10-25% mica, and 6-65% quartz. In addition, there are other 'accessory' minerals and some carbonaceous material (derived from ancient plants) present. The wide variation both in mineral composition and in the size of the clay particles results in different characteristics for individual clay seams within a deposit.*



**British
Geological Survey**

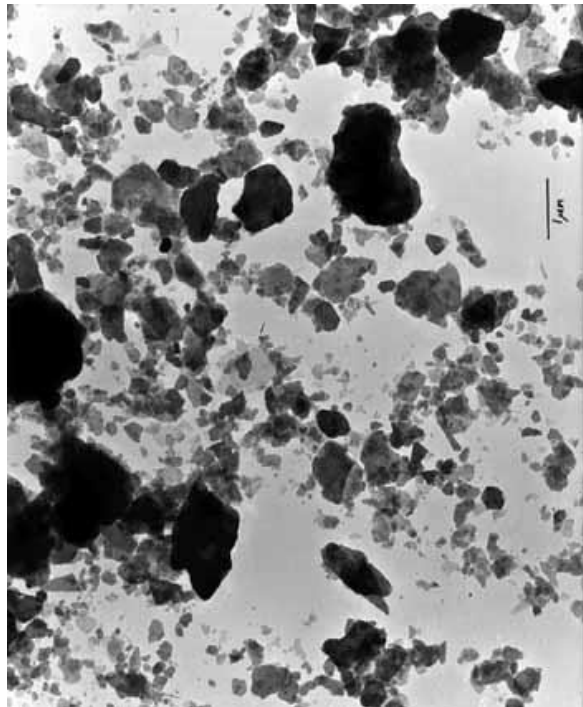
NATURAL ENVIRONMENT RESEARCH COUNCIL

Mineral Planning Factsheet

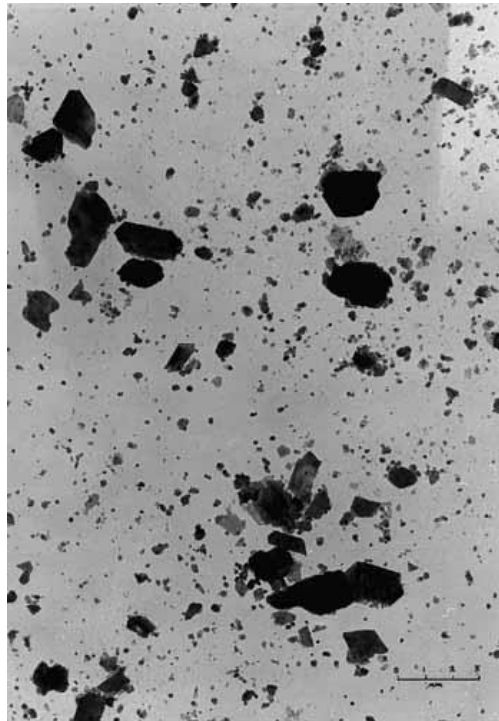
Ball clays are fine-grained, highly plastic sedimentary clays, which fire to a light or near white colour. They are used mainly in the manufacture of **ceramic whiteware** and are valued for their key properties of plasticity, which makes them easy to mould, their unfired strength and the fact that when fired they have a light colour. Normally sedimentary clays fire to a reddish colour. Some ball clays are also valued for their ability to readily disperse in water to produce fluid slips (high solids aqueous suspensions). Ball clays exhibit highly variable compositions and consist not of a single mineral but a mixture of mainly three minerals; kaolinite, mica and quartz, with each mineral contributing different properties to the clay. The clay mineral **kaolinite** is the key component. The crystallinity of the kaolinite, in terms of being well-ordered (less plastic and coarser) or disordered (highly plastic and fine grained) also has a marked influence on ceramic performance.

Janaury 2006

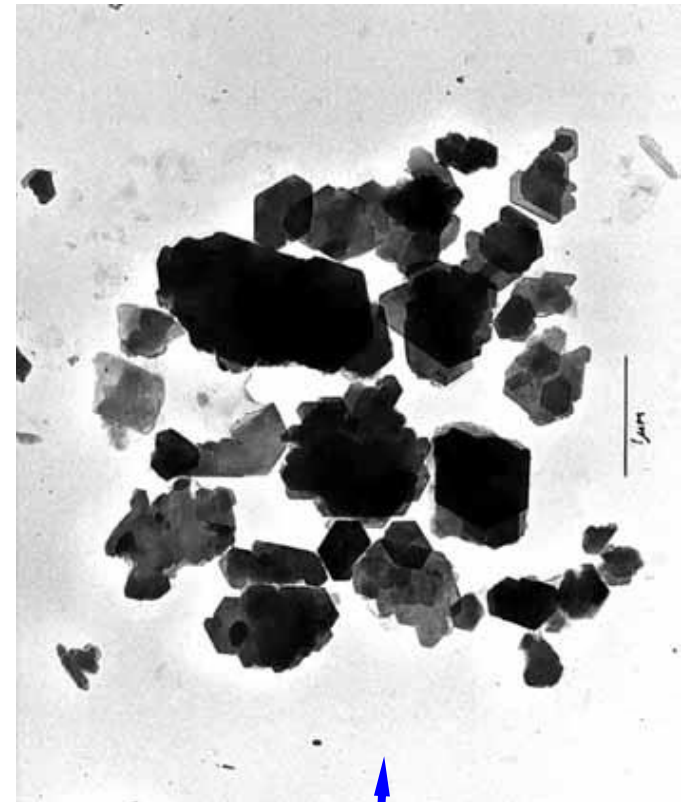




*MET de "ball clay" de
Devon (UK) , mostrando
os cristais de caulinita
com baixa cristalinidade*



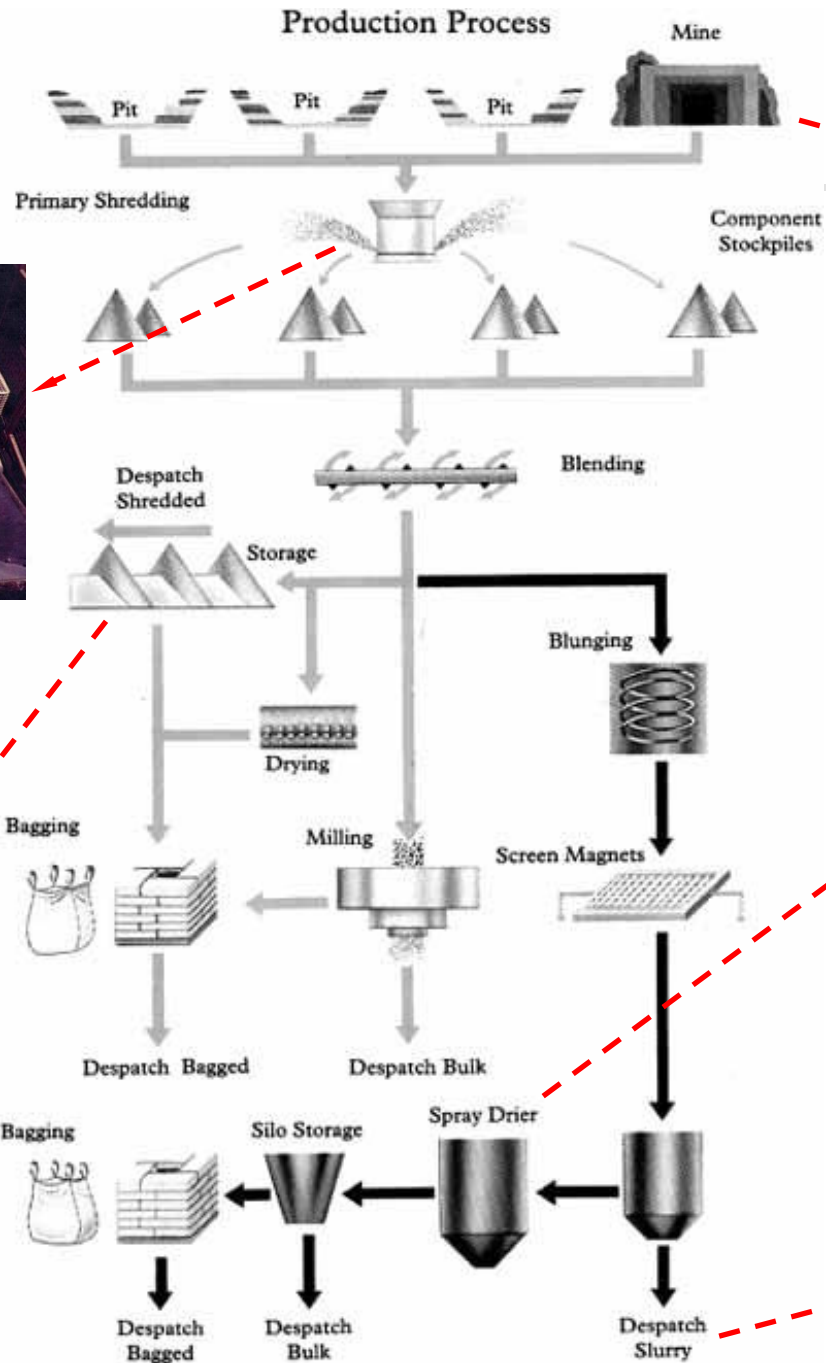
*MET de "ball clay" de
São Simão (SP)*



*MET de caulim típico de Cornwall (UK) ,
("Cornish China clay") mostrando
os cristais de caulinita
com elevada cristalinidade*



Esquema geral
de processamento
de "ball clay"





Aplicações Industriais de “ball clays”

- Matéria-prima para produtos cerâmicos
 - Louça de mesa
 - Louça sanitária
 - Refratários
 - Revestimentos cerâmicos
 - Porcelana para uso elétrico
- Aditivos (“*extenders*”) para polímeros e adesivos
- Componentes para fabricação de agentes selantes, fertilizantes e inseticidas



"Ball Clays" no Mundo

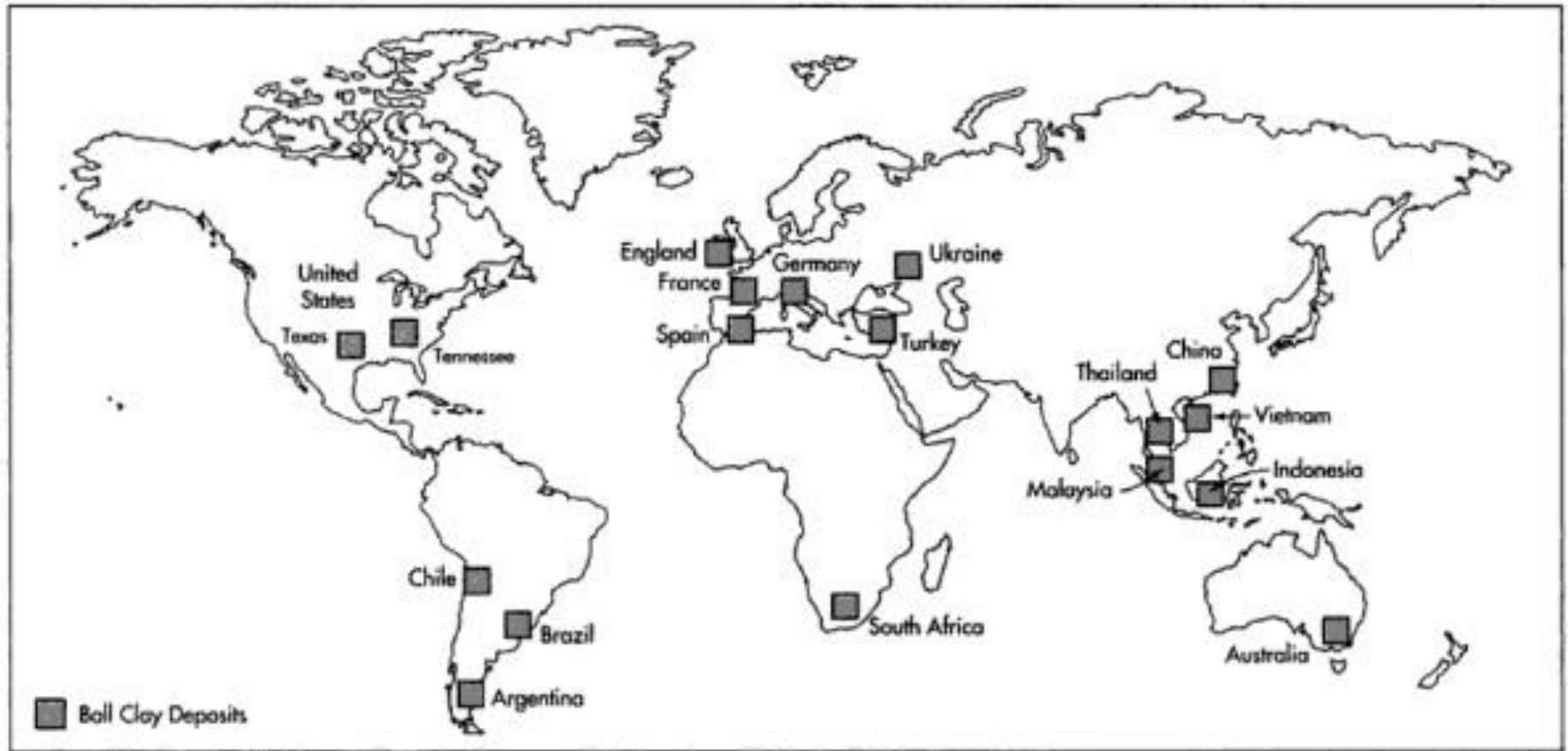


Figure 1. Map of some major ball clay deposits of the world



"Ball Clays" na Europa



Figure 13. Map of the ball clay deposits of Europe



"Ball Clays" na Ásia



Figure 14. Producers of some ball clay deposits in Asia



"Ball Clays" no Brasil



SAO SIMAO

0 100km
scale



Sao Paulo



SUZANO

RIBEIRAO PIRES

Min. Tabatinga
(50km S. of Curitiba)

Ball Clay Deposits

SKETCH MAP OF BALL CLAYS
IN THE VICINITY OF SAO PAULO





Haloisita

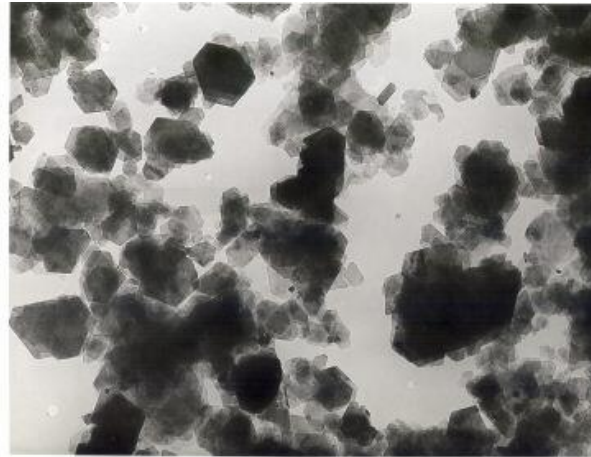
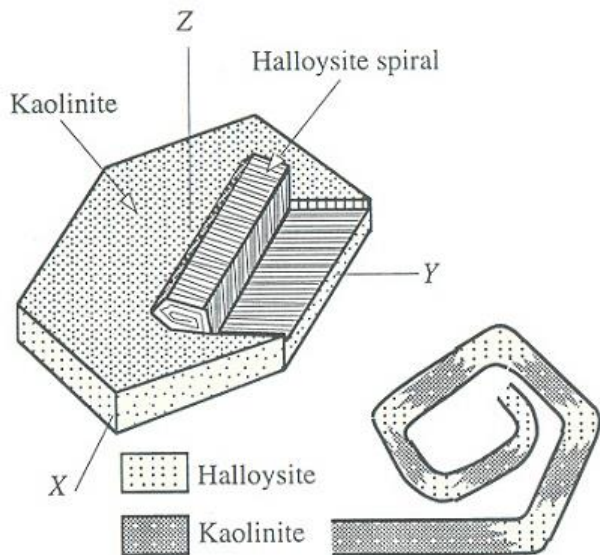
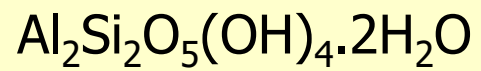
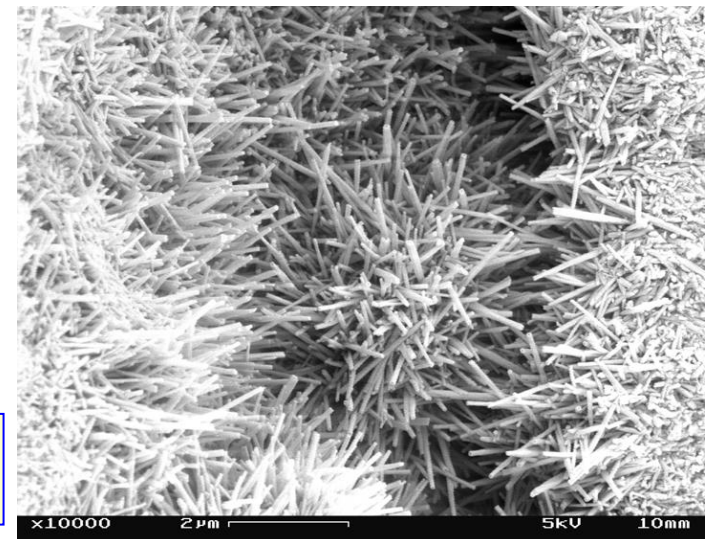


Imagem de MET
de caulim caulínítico

Imagem de MEV de haloisita do noroeste da Turquia.
Origem: alteração hidrotermal de andesita





Halloisita

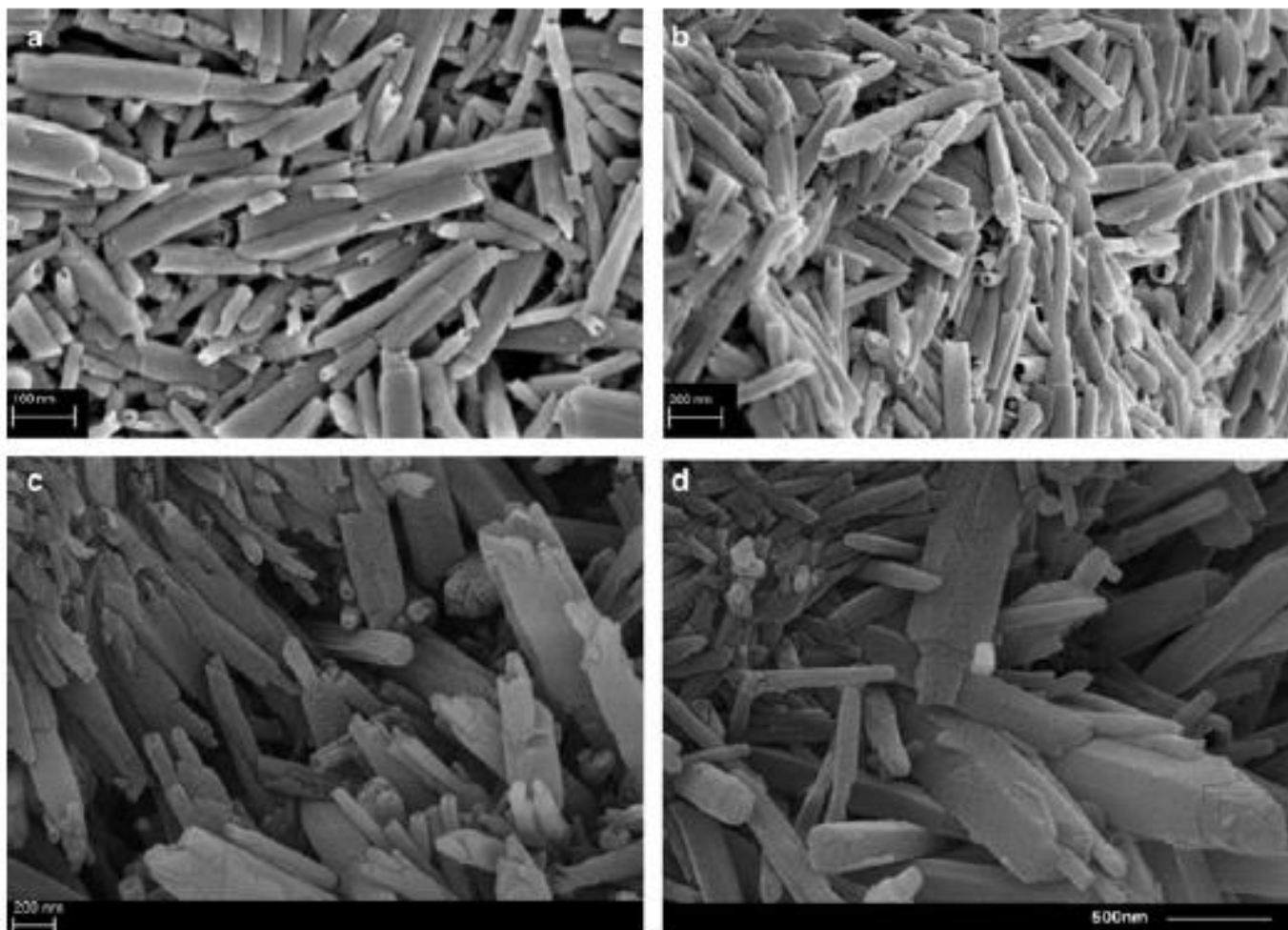


FIG. 3. SEM images of varying morphologies of halloysite from Dragon mine, Utah. (a) Cylindrical tubes – underground from J1 location. (b) Cylindrical tubes – underground 300 ft level. (c) Cylindrical and polygonal tubes – Dragon pit centre outcrop. (d) Polygonal tubes – diamond drill hole 4-2009, 235 ft.



Haloisita

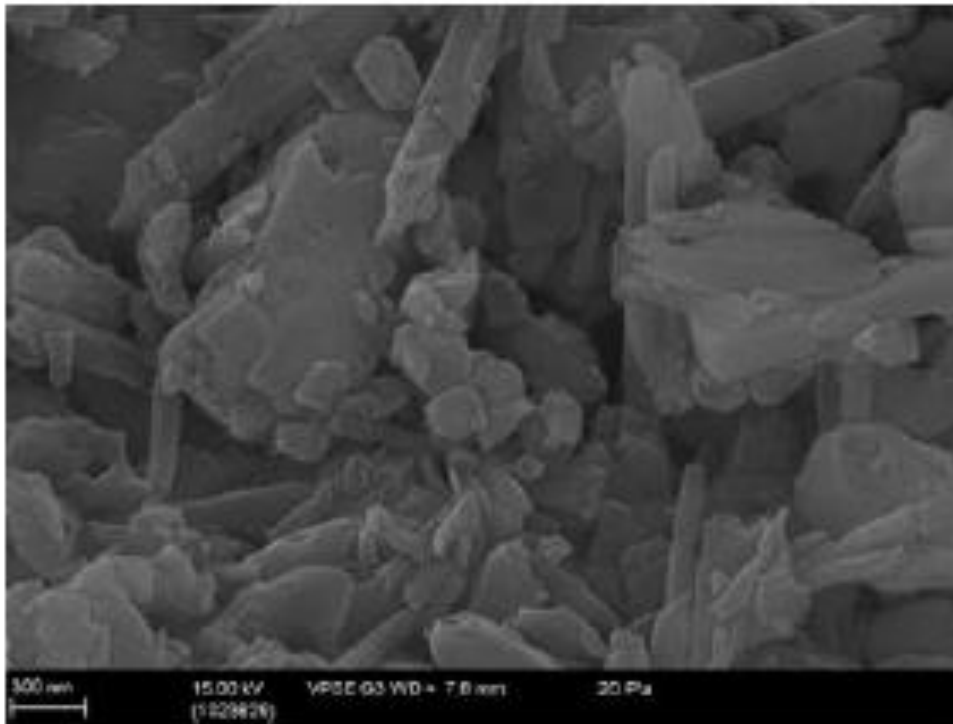


FIG. 7. SEM image of haloisite from Matauri Bay, Northland, New Zealand

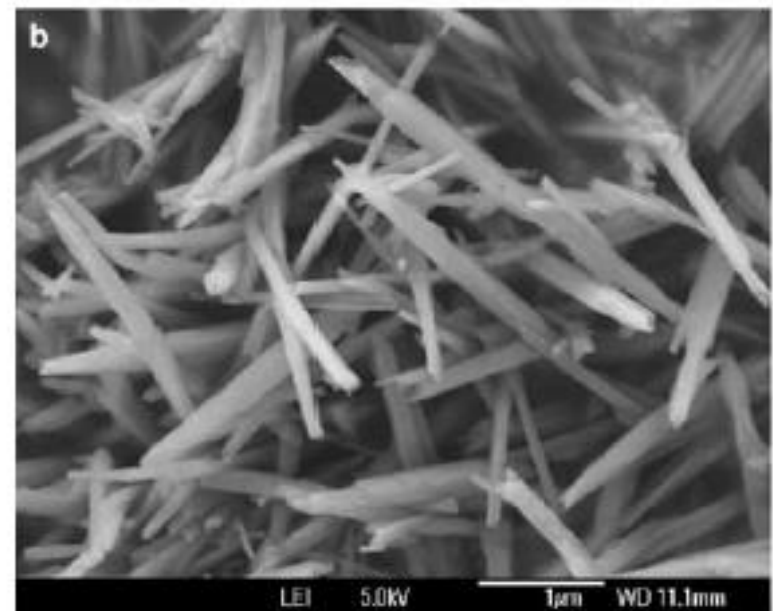
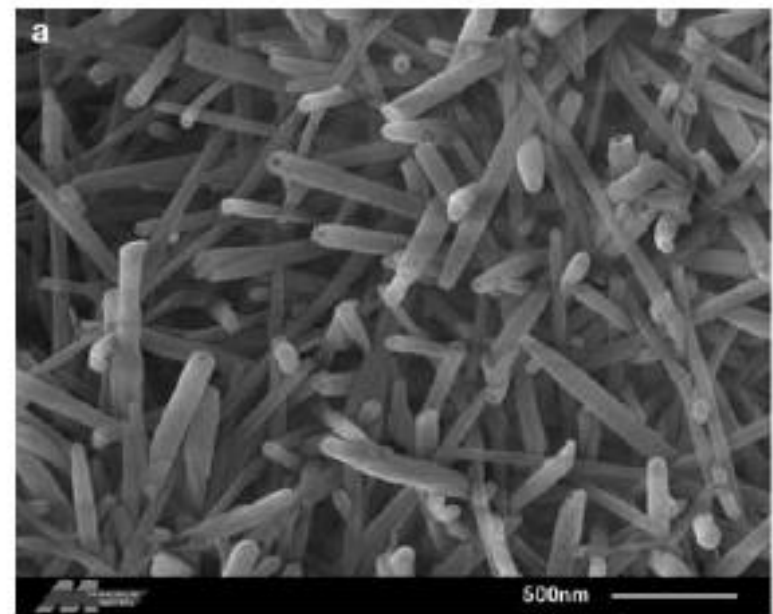


FIG. 4. SEM images of: (a) haloisite with tubular cylindrical morphology from Dafang haloisite, Guizhou; and (b) haloisite with tubular prismatic/polygonal morphology from Yiliang haloisite, Yunnan.



Halloysita

TABLE 1. Some properties of tubular halloysite.

Property	Details
Chemical formula	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O} / \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Hydrated halloysite	10 Å Halloysite
Dehydrated halloysite	7 Å Halloysite
Molecular weight	294.2 (hydrated), 258.2 (dehydrated)
CAS Registry Number	1332-58-7
Density (gm/cm^3)	2.1 (hydrated)–2.6 (dehydrated)
Hardness (Moh's)	1–2
Refractive index	1.534
Tubular shape maintained until	900°C
Cation Exchange Capacity	5 to ~20 meq/100 g
Morphology	Tubular-cylindrical and polygonal
Range of size of tubes	Lumen diameter = 5–30 nm Outer diameter 50–200 nm (0.05–0.20 μm) Length 50–30,000 nm (0.05–30 μm)
BET surface area	23–89 $\text{m}^2 \text{g}^{-1}$
Transparency	Colourless, UV transparent

TABLE 5. Some present and future uses and applications for halloysite.

Market sector	Present and future uses and applications for halloysite
Controlled release	Halloysite nanotube (HNT): compounds can be loaded into tubes and released at a predictable rate
Environmental remediation	Sequester pollutants from oil spills, power plants and mine sites. Used for oil, toluene, phenols, heavy metals and uranium
Oil remediation	Deep-water environment: absorbed de-emulsified and dispersed micro-droplets of oil will float Will absorb and with action of bacteria, 98% of the oil will degrade within 7 days Marshland Environment: will absorb oil and will prevent penetration to subsurface
Agriculture	Can load, store and release agricultural agents uniformly. Avoids need for frequent spraying. Agents for pesticides, fertilizers, insecticides, fungicides, herbicides, vitamins and hormones Applications: crops, tree crops, plants, shrubs, trees and control of fleas and ticks on animals
Paint and Coatings	Loading of biocides for sustained release protection against microbial growth and corrosion
Fluid Cracking Catalysts (FCC)	Used in conversion of gas, oils and residues to light olefin, high octane and distillates Tubular shape, pore-size, thermal stability and large surface area ideal to remove impurities
Catalysts	Molecular sieves: binder for zeolites to enhance drying of natural gas and air separation of liquid Hydrocracking Catalysts and supports: removes impurities such as metals, sulfur, nitrogen
Polymer Composites	1% in polypropylene (PP) improves mechanical properties with modulus increased by 20–25% Strength increased by >20% and impact resistance increased by 40%. Cycle-time reduced by 15%. Effective in processing of injection and blow moulding, automotive parts and household appliances. Loading of 1% in polyethylene (PE) similar to improvements in PP
Flame retardant plastics	Halloysite (15% lattice water) not released until 400°C – good for plastic processed at higher temperature Can be used as stand-alone or in conjunction with flame retardant components
Cosmetics	White, pure halloysite performs as a non-irritating skin cleanser with cosmetic agents added to tube. Possibilities include skin and sun care, hair, oral, colour cosmetics, detergents and bug repellents
Ceramics	Porcelain/Bone China – low iron and titania on firing body will give good translucency Fine particle size halloysite has significant strength and is used to blend with kaolin in ceramic bodies Sanitaryware – halloysite with long tubes often have good casting properties. Other markets.
Pharmaceuticals	Appropriate drugs loaded into halloysite tubes (HNT) and are released at a constant rate. Non-toxic Loaded with antibacterial and antiseptic agents, enzymes and proteins. Sustained-released capsules



- Dragon Mine, Utah (USA)
- Guizhou, Yunnan e Hunan (China)
- Biga (Turquia)
- Kerikeri-Matauri Bay (Nova Zelândia)

<http://www.mindat.org/min-1808.html>

Wilson, I.; Keeling, J. Clay Minerals **51** (3), 309-324 (2016)

<https://www.imerys-ceramics.com/halloysite>



TABLE 4. Some halloysite and mixed halloysite-clay deposits.

Country	Company/ Location	Type of deposit	Mineralogy	Markets	Capacity (tpa)
Argentina	Piedra Grande, Chubut Province	Altered volcanics	Halloysitic clay	Mainly ceramics	25,000
Australia	Minotaur, Poochera, South Australia	Altered granite	Kaolinite + Halloysite	Ceramics and fillers	Pilot plant
	Maralinga, Camel Lake, South Australia	Altered clay sediment	Halloysite		Prospect
Brazil	Various, Minas Gerais	Altered pegmatites	Halloysite + Kaolinite	Fillers, ceramics	50,000
	Ceramica Oxford, Santa Catarina	Altered rhyolites	Halloysite + Kaolinite	Ceramics	40,000
	Mineração Horii, Jundiapéba, SP	Altered granite	Kaolin + Halloysite	Fibre glass, ceramics	80,000
	Various, Encruziilhada, RGS	Altered anorthosite	Halloysite + Kaolinite	Ceramics, fillers	—
China	Longyan Kaolin, Longyan, Fujian	Altered granite	Kaolin + Halloysite	Ceramics – porcelain	50,000
	China Clay Co, Suzhou, Jiangsu	Altered volcanics	Mainly Halloysite	Mainly ceramics	100,000
	Changning, Jiepai, Liling, Hunan	Altered granites	Kaolin + Halloysite	Mainly ceramics	100,000
Mexico	Various locations	Altered volcanics	Halloysite + Kaolin	Ceramics	
Poland	KH Dunino Sp, Krotoszyce, Legnica	Weathered basalt	Kaolinite + Halloysite	Absorption, liners	3000
South Korea	Various, Handong-Sancheong area	Altered anorthosite	Mainly Halloysite	Ceramics	
Thailand	Imerys-MRD, Ranong Province	Altered granite	Mainly Halloysite	Sanitaryware,	73,000
USA	IM-Minerals, Bovil deposit, Idaho	Weathered granite	K-feldspar, halloysite	Being studied	Not known