

DISSOLUTION KINETICS OF KAOLIN

IN CAUSTIC LIQUORS

G.I.D. Roach and A.J. White

Research and Development Department

Alcoa of Australia Limited

Kwinana, Western Australia

Kaolin is the most common form of reactive silica in bauxite. To better understand the behaviour of kaolin in the Bayer process, the dissolution kinetics of kaolin in caustic liquors were studied. The kaolin samples used were two forms of pure kaolin, clay samples from bauxite mining areas and the reactive silica in bauxite. Dissolution in both synthetic and plant caustic liquors was investigated at temperatures from 65 to 150°C. Particle size had little effect on dissolution rate; the kaolin particles were porous and reacted both internally and externally. Kaolins which contained halloysite dissolved faster. The activation energy obtained was 93kJmol^{-1} for the pure kaolins and a similar value for the reactive silica in bauxite. The dissolution rate increased proportionally to the free caustic concentration, and decreased with increasing alumina and silica concentrations. Sodium carbonate did not affect the dissolution rate. The precipitation of desilication product from the liquor did not affect the rate of kaolin dissolution. The dissolution rate of kaolin is sufficiently slow that it can affect the level of desilication achieved in low temperature digest Bayer refineries.

INTRODUCTION

Kaolin, a hydrated aluminium silicate, is the predominant reactive silica component in most bauxites used in the Bayer process. The kaolin dissolves in the caustic liquor together with the gibbsite; subsequently the silica precipitates as a desilication product, DSP (a hydrated sodium aluminium silicate). The kaolin dissolution and subsequent DSP precipitation is commonly referred to as desilication.

The desilication occurs primarily either within predigestion desilication tanks or in the Bayer digesters. The typical profile of silica concentration in the liquor for the desilication process is shown in Figure 1. There is an increase in silica concentration as the kaolin dissolves. Once a certain level of silica in solution is reached, the DSP nucleates and subsequently the silica concentration drops. The final silica concentration in the liquor directly affects the level of silica in the product alumina. There have been numerous papers published on the desilication process and, in particular, the modelling of the process (e.g. Oku and Yamada, 1971; Pevzner et al, 1975; Ni et al, 1978; Cresswell, 1984). Virtually all such papers and models have concentrated on the DSP precipitation reaction, i.e. the removal of

silica from the liquor. Invariably the desilication of the liquor is considered to be independent of the dissolution reaction, yet many of those papers present the desilication process as in Figure 1. The final part of the kaolin dissolution curve is shown as a mirror image of the drop of silica concentration in the liquor. Such data suggest that the kaolin dissolution rate has a major effect on determining the level of silica in solution. Kaolin dissolution is not necessarily rapid; one variant of the Bayer process which has been proposed utilises the slow dissolution kinetics of kaolin (Grubbs, 1987). In that process the bauxite is digested under atmospheric digest conditions for a short period (105°C for 30 minutes); all the gibbsite is extracted but only part of the kaolin is attacked. The residue is separated from the liquor and then further bauxite is charged to the liquor at the normal digest temperature of 143°C; this double digest procedure reduces the fixed soda loss.

Alcoa of Australia Limited processes bauxite from the Darling Range, Western Australia, in which the majority of the silica in the bauxite is coarse-grained quartz (about 20wt% of the bauxite). Little of that quartz dissolves in the low temperature (145°C) digest conditions used. The reactive silica level of the bauxite is about 1.3%SiO₂ and the major forms of reactive silica are the kaolin minerals. The low level of reactive silica makes tight control of refinery digest conditions essential in order to achieve the necessary silica level in the final green liquor. (For bauxites with a higher level of

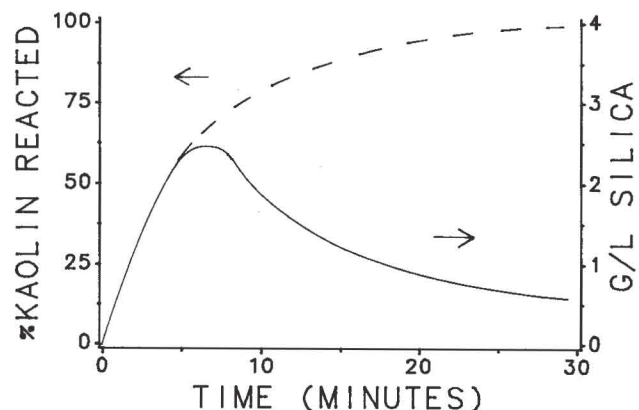


Figure 1 - Desilication in Bayer liquor showing kaolin dissolution and the change in silica concentration of the liquor during digestion.

reactive silica, more DSP seed is formed during digestion and consequently the silica in the liquor precipitates more rapidly.)

Because of the need for tight control over the desilication process, studies were undertaken to construct a deterministic model of desilication. Such deterministic models not only enable optimisation of the process, but can be extrapolated more successfully than empirical models to new conditions, e.g. new liquor conditions, different bauxites and different reactive silica levels in bauxite, etc.. For such a deterministic model of desilication, it is necessary to have kinetic information on both the dissolution reaction as well as the DSP precipitation reaction. Unfortunately little data have been published on the kinetics of kaolin dissolution in caustic liquors. Oku and Yamada (1971) studied the dissolution of quartz in some detail, but not kaolin. In this paper dissolution data for several different kaolin samples in caustic liquor are presented. The effects of both mineralogical and chemical factors were studied. Also, the questions of whether precipitation of DSP affects kaolin dissolution, and whether kaolin dissolution can affect the final silica concentration of the liquor, are assessed.

EXPERIMENTAL

Four kaolin samples were used in this study: a pure kaolin (D2) from Greenmount (Western Australia), a filler clay (essentially pure kaolin) and two clays from the Jarrahdale minesite of Alcoa of Australia Limited. The two minesite clays were of pegmatite/granite and dolerite origin, containing reasonable levels of impurities (approximately 10wt%); the major impurities were quartz (coarse-grained), gibbsite and iron oxides. A typical bauxite sample from the Jarrahdale minesite was also used, the reactive silica in that bauxite would be predominantly a mixture of the minesite clays tested. Wet screening was used to obtain various size fractions. X-ray diffraction analysis was used to confirm that kaolin was the primary reactive silica mineral. The B.E.T. surface area of selected size fractions of the D2 kaolin and filler clay were determined using nitrogen adsorption (single point method).

The sized samples were used for comparisons of the clay types and to determine the effect of particle size. For the remainder of the work, finely pulverised samples of either D2 kaolin or filler clay were used. The standard dissolution condition used to determine the effects of mineralogy and particle size on the dissolution kinetics of the kaolin samples was dissolution at 95°C in a synthetic sodium hydroxide solution containing 106gL⁻¹ free caustic. All free caustic concentrations are expressed as gL⁻¹ Na₂CO₃. The effect of temperature on the dissolution was studied over the range 65 to 150°C. The start liquor composition was altered to determine the effects of free caustic, alumina, silica and sodium carbonate concentrations on the rate of dissolution. The free caustic concentration was varied from 26 to 106gL⁻¹, the alumina concentration from 0 to 10gL⁻¹ Al₂O₃ (by dissolving sodium aluminate), the silica concentration from 0 to 12gL⁻¹ SiO₂ (by dissolving sodium silicate) and the sodium carbonate concentration from 0 to 40gL⁻¹ Na₂CO₃. Tests were also undertaken using spent liquor from the Alcoa of Australia Limited Kwinana refinery, the alumina concentration being varied from 60 to 110gL⁻¹.

The digests were carried out in a 3-litre stirred reactor for temperatures below 100°C, and in a 1-litre autoclave for the higher temperatures. The kaolin was charged into the reactor at temperature; for the autoclave digests the kaolin was contained in a sealed sample holder inside the autoclave, the holder being opened to initiate the dissolution. Kaolin was charged to give a final silica concentration of 1gL⁻¹ SiO₂ except as otherwise stated for specific tests; at that silica level there was no precipitation of DSP during dissolution. That charge level ensured little change in caustic concentration of the liquor during dissolution. The dissolution was monitored by removing liquor aliquots at set time intervals; the liquor was analysed for silica by the molybdenum-blue spectrophotometric method. An alternative method was required for dissolutions in refinery liquors as the high alumina and silica levels result in DSP precipitation. The kaolin and liquor were mixed in 200mL polypropylene bottles, sealed, and placed in a rotating carousel sample holder which was immersed in a water bath. At set time intervals a bottle was removed, cooled, and the contents filtered. The liquor was analysed for silica as above. The solids were washed, dried, then leached with dilute sulphuric acid to dissolve any DSP precipitated. That silica was then measured using the molybdenum-blue spectrophotometric method. This bottle method gave identical dissolution curves to those obtained by the reactor method.

RESULTS

Dissolution Curves

Typical dissolution curves for three kaolin types at 95°C in 106gL⁻¹ free caustic solution are shown in Figure 2. All dissolution curves were essentially concave to the time axis. The dissolution curves were quite reproducible. Initial testwork indicated that the dissolution was not affected by a change in the reactor stirrer speed. For one dissolution run both the silica and alumina concentrations were measured; the two analyses gave identical dissolution curves and the ratio of silica to alumina was consistent with kaolin dissolving. In another test, coarse (130µm) particles of D2 kaolin were digested at 95°C in 106gL⁻¹ free caustic to 50% reaction. Examination of the undigested kaolin indicated some of the particles had disintegrated; however, the majority of the kaolin was present as smaller, but discrete particles (Figure 3).

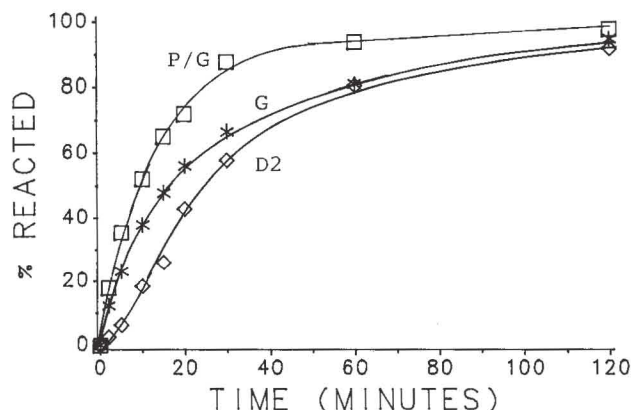


Figure 2 - Dissolution curves for three of the kaolin types digested in caustic liquor at 95°C.

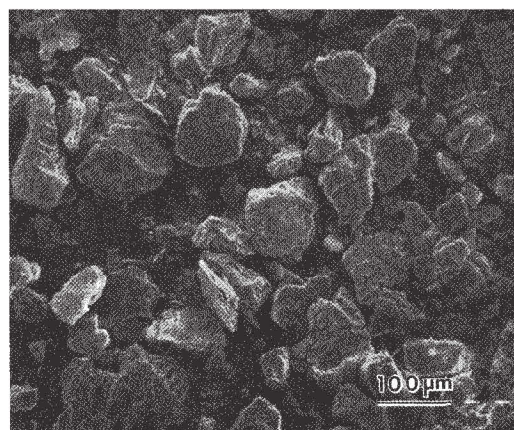
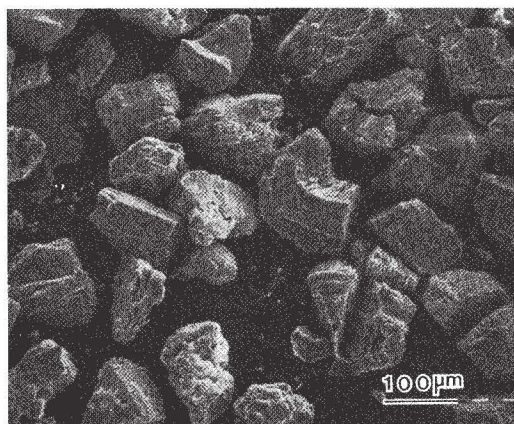


Figure 3 - Undigested (upper) and part digested (lower) particles of D2 kaolin. Little disintegration of the particles has occurred.

The dissolution curves were characterised by the dissolution rate at 20% reaction, i.e. the slope of the tangent to the dissolution curve at the point where 20% of the kaolin had reacted. This rate, rather than the initial rate, was chosen because the 20% rate could be determined more accurately. The experimental error in the rate parameter was 10-20% of the measured value, the greater error being for runs above 100°C. The derived rates for all of the dissolution curves are given in Tables 1 and 2. These rates were used to evaluate and quantify the effects of the various parameters on the dissolution rate.

Effect of Kaolin Type

Dissolution curves for 170µm sized particles of three of the kaolins are presented in Figure 2. The dissolution rates at 20% reaction for the minesite clays were up to two times faster than that for the D2 kaolin. For the two pure kaolin samples, the D2 kaolin dissolved approximately 1.4 times faster than the filler clay at all temperatures studied. The D2 clay had a higher surface area than the filler clay, 16m²g⁻¹ compared to 8m²g⁻¹. Electron microscope examination indicated that in D2 kaolin both kaolinite (platy) and halloysite (tubular) forms of kaolin were present (Figure 4); the filler clay contained only the platy kaolinite. For D2 kaolin, the kaolinite platelets were about 20µm in size and often occurred in book form; the halloysite tubes were approximately 3µm long and 0.2µm in diameter.

Examination of the part-digested D2 kaolin indicated that the halloysite dissolved more rapidly than the kaolinite. The x-ray diffraction data for these two clays indicated that the filler clay had a higher degree of preferred orientation and a more intense 10Å reflection. For the part-digested residue of D2, the x-ray diffraction data were more similar to those for the filler clay. This suggests that the less crystalline and less-platy crystallites of kaolinite dissolved more rapidly. No attempt was made to quantify the relative amounts of kaolinite and halloysite by either microscopy or x-ray diffraction.

Table I. Reaction Rates at 20% Reaction, Dissolution of Kaolin in Synthetic Caustic Solutions, %·min⁻¹

KAOLIN TYPE	T, °C	PARTICLE SIZE, µm			
		18	40	170	150
D2 KAOLIN	95			2.53	1.59
FILLER CLAY	80	0.25	0.20		
DOLERITE CLAY	95			3.33	
PEGMATITE/ GRANITE CLAY	95			6.00	

	TEMPERATURE, °C				
	65	80	95	120	150
D2 KAOLIN	0.11	0.46	1.74	10.9	89.9
FILLER CLAY	0.06	0.37	1.12	8.10	85.8
BAUXITE	0.12	0.66	2.13		

	CAUSTIC CONCENTRATION, gL ⁻¹ Na ₂ CO ₃			
	26	53	80	106
D2 KAOLIN	0.38	1.05	1.21	1.88

	SILICA CONCENTRATION, gL ⁻¹ SiO ₂					
	0	3.7	6.3	9.2	12.7	25.4
D2 KAOLIN	80	0.46	0.16	0.07	0.05	0.04
D2 KAOLIN	120	10.9	7.47	4.58		1.74
D2 KAOLIN	150	89.9	79.6	37.8		27.7

	ALUMINA CONCENTRATION, gL ⁻¹ Al ₂ O ₃			
	0	3.3	6.5	9.8
D2 KAOLIN	95	1.88	1.16	1.05
				0.88

	CARBONATE CONCENTRATION, gL ⁻¹ Na ₂ CO ₃	
	0	40
D2 KAOLIN	80	0.46
		0.52

Table II. Reaction Rates at 20% Reaction for Dissolution of Kaolin in Refinery Liquor at 95°C

D2 KAOLIN			BAUXITE		
CAUSTIC gL ⁻¹	ALUMINA gL ⁻¹	RATE %.min ⁻¹	CAUSTIC gL ⁻¹	ALUMINA gL ⁻¹	RATE %.min ⁻¹
84	57	1.05	77	65	1.65
127	57	1.60	116	66	2.75
168	57	2.20	157	66	3.40
111	62	1.30	102	70	2.15
111	82	1.11	102	90	2.09
111	102	1.06	102	110	1.97

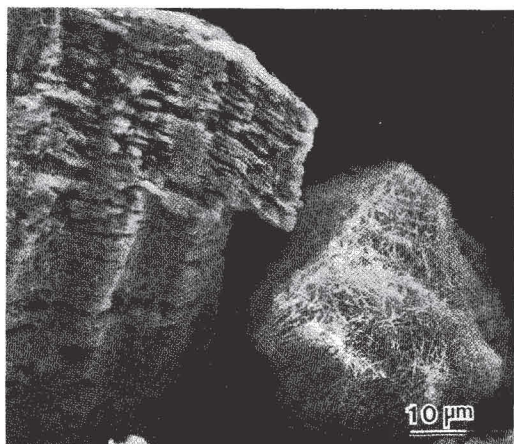


Figure 4 - Particles of D2 kaolin. The particle on the left is predominantly kaolinite, the one on the right consists entirely of halloysite.

Effect of Particle Size

The dissolution of 170 μm and 650 μm sized particles of D2 kaolin at 95 $^{\circ}\text{C}$, and 18 μm and 40 μm filler clay at 80 $^{\circ}\text{C}$, in 106 gL^{-1} free caustic solution, was studied. The difference in the rate parameter for the two particle sizes of D2 kaolin was a factor of 1.6; a four-fold difference would have been expected if the particles were dissolving topochemically. For the two sizes of filler clay there was essentially no difference in the rate; a two-fold difference would have been expected based on particle size. The surface areas for the 18 μm and 40 μm sizes of filler clay were very similar, 10 m^2g^{-1} and 8 m^2g^{-1} respectively. The high surface area values indicate that the particles have a high degree of internal surface area. Clearly the data indicate that the particle size of the kaolin has little effect on the dissolution rate.

Effect of Temperature

The effect of temperature on the dissolution rate for the D2 and filler clays was studied from 65 to 150 $^{\circ}\text{C}$ in 106 gL^{-1} free caustic solutions. The rate data are presented as Arrhenius plots in Figure 5. The plots for the two kaolin types are linear, and the slopes of the lines are essentially the same.

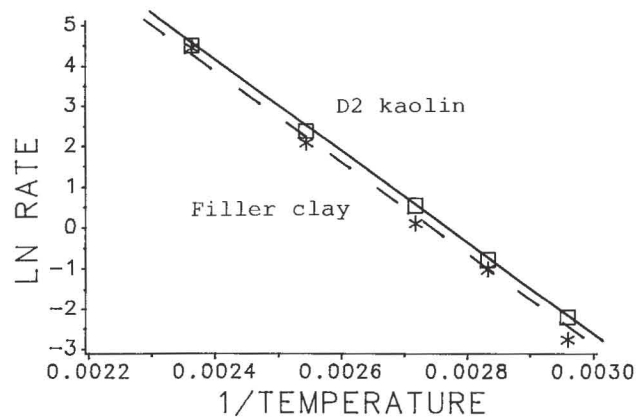


Figure 5 - Arrhenius plots for D2 kaolin and filler clay digested in synthetic caustic liquor.

The activation energy obtained from the slopes was 93 kJmol^{-1} . The effect of temperature for the reactive silica in bauxite was studied over the range from 65 to 95 $^{\circ}\text{C}$. Although there was more scatter in the data, the plot was linear and an activation energy of 99 kJmol^{-1} was obtained. This value is, within experimental error, consistent with that obtained for the pure kaolins. The high activation energy, the lack of an effect of agitation on the dissolution rate, and the long dissolution times are all consistent with a reaction controlled by the rate of chemical reaction at the mineral surface. Even at the highest temperature studied, 150 $^{\circ}\text{C}$, the dissolution was still not affected by diffusion control considerations.

Effect of Liquor Composition

The effects of free caustic, alumina, silica and carbonate concentrations in the liquor on the rate of dissolution were studied using primarily the D2 kaolin. The effect of liquor composition on the rate of reaction should be independent of the mineralogy of the kaolin.

The effect of the free caustic concentration on the dissolution rate is shown in Figure 6 for a 95 $^{\circ}\text{C}$ digest. The free caustic concentration had a major effect on the rate; a change in concentration from 26 to 106 gL^{-1} free caustic increased the rate by a factor of 5. A linear relationship is indicated and the line can readily be made to pass through the origin.

The effect of the silica concentration on the dissolution rate is shown in Figure 7 for an 80 $^{\circ}\text{C}$ digest. The initial silica concentration was varied from 0 to 25 gL^{-1} SiO_2 . (The dissolution of the kaolin did not change the silica concentration by more than 1 gL^{-1} SiO_2 .) The silica concentration clearly had a marked effect on the dissolution rate; an increase in silica from 0 to 5 gL^{-1} decreased the rate by a factor of about 0.2. Similar effects of silica on the rate were found at 120 $^{\circ}\text{C}$ and 150 $^{\circ}\text{C}$. The scatter in the data made it difficult to define the order of reaction; values between -0.3 and -1.0 were obtained. No further work was undertaken as the silica concentration in plant liquor varies relatively little, hence the silica effect did not need to be defined precisely.

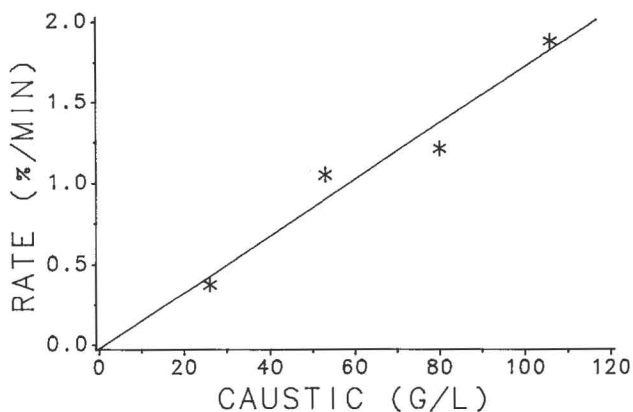


Figure 6 - Effect of free caustic on the rate for D2 kaolin at 95 $^{\circ}\text{C}$.

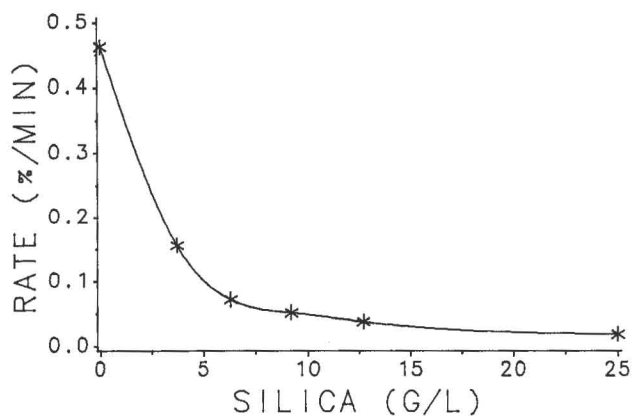


Figure 7 - Effect of silica on the rate for D2 kaolin at 80°C in 106gL⁻¹ free caustic.

The effect of alumina concentration on the dissolution rate is shown in Figure 8 for a 95°C digest (broken line). The alumina concentration was varied from 0 to 10gL⁻¹ Al₂O₃ with a constant free caustic concentration of 106gL⁻¹. The alumina concentration had a strong effect on the dissolution; a change from 0 to 10gL⁻¹ Al₂O₃ decreased the rate by a factor of 0.6. In other work the alumina concentration was varied from 0 to 70gL⁻¹ for digests at temperatures from 80 to 150°C. The alumina was varied by dissolving aluminium hydroxide, extra sodium hydroxide was not added. Consequently, the free caustic concentrations were lower at the higher alumina concentrations. The kaolin dissolution rate decreased markedly with increasing alumina concentration. When allowance was made for the effect of the change in free caustic, the alumina concentration still had a major effect. A change in alumina concentration from 0 to 10gL⁻¹ decreased the rate by a factor of 0.5 and from 0 to 70gL⁻¹ by a factor of 0.2. The data are also presented in Figure 8 (solid lines). The order of the effect was about -0.3 at each temperature.

The effect of carbonate was assessed by adding 40gL⁻¹ sodium carbonate to the start liquor (106gL⁻¹ free caustic solution). There was no significant change in the rate of dissolution.

Kaolin Dissolution in Refinery Spent Liquor

For these dissolutions the bottle method described previously was used because of the precipitation of the desilication product. A typical composition of the refinery liquor is 190gL⁻¹ total

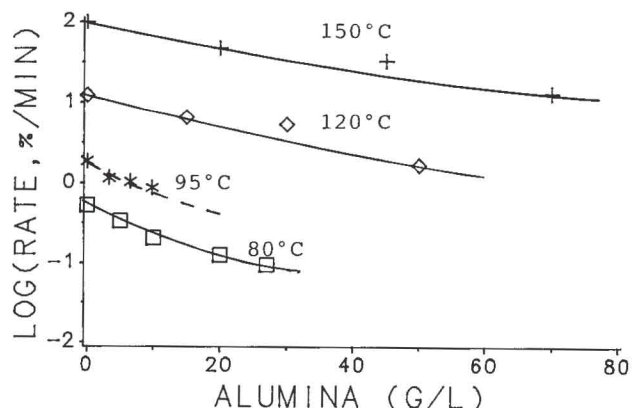


Figure 8 - Effect of alumina on the rate for D2 kaolin in 106gL⁻¹ free caustic.

caustic, 235gL⁻¹ total alkali, 0.66gL⁻¹SiO₂, 80gL⁻¹ Al₂O₃ and 30gL⁻¹ total organic carbon. Hence the liquor has a free caustic concentration of 110gL⁻¹. The liquor was adjusted to give a range of free caustic concentrations from 84 to 168gL⁻¹ at a fixed alumina concentration of 57gL⁻¹. The rate data for D2 kaolin are presented in Figure 9. A linear relationship is indicated and the line can readily be made to pass through the origin. The slope was less than that obtained for D2 kaolin in synthetic liquor by a factor of 0.7. However, the refinery liquor contained 57gL⁻¹ Al₂O₃. To determine the effect of alumina, the liquor was adjusted to give concentrations from 62 to 102gL⁻¹ Al₂O₃ at a fixed free caustic concentration of 111gL⁻¹. Alumina had only a small effect on the dissolution rate; a change in concentration from 62 to 102gL⁻¹ Al₂O₃ decreased the rate by a factor of only 0.8. The effect of silica concentration was not studied as little change in silica concentration occurs in refinery liquors.

Bauxite Reactive Silica Dissolution in Refinery Spent Liquor

A bauxite charge equivalent to the reactive silica content of the standard D2 kaolin charge was used in these digests. To determine the effect of free caustic, the liquor was adjusted to give free caustic concentrations from 77 to 157gL⁻¹ at a fixed alumina concentration of 65gL⁻¹. The rate data are presented with the D2 kaolin data in Figure 9. A linear relationship is again indicated with free caustic, and the line can readily be made to pass through the origin. The slope was nearly twice that obtained for D2 kaolin in refinery liquor. For the effect of alumina, the liquor was adjusted to give alumina concentrations from 70 to 110gL⁻¹ Al₂O₃ at a fixed free caustic concentration of 102gL⁻¹. There was little effect on the dissolution; the change in concentration from 70 to 110gL⁻¹ Al₂O₃ decreased the rate by a factor of only 0.9.

DISCUSSION

Effect of Kaolin Mineralogy on the Dissolution Rate

The different kaolin samples, including the reactive silica component of the bauxite sample, had quite different dissolution rates under similar reaction conditions. The differences in rate were related to both the surface area of the kaolins and the specific form of kaolin: kaolinite or halloysite. For kaolin samples which contained both minerals, the halloysite dissolved more readily. The

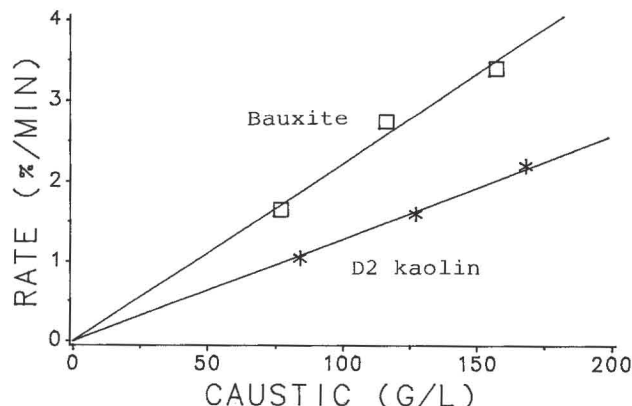


Figure 9 - Effect of free caustic on the rate for D2 kaolin and bauxite reactive silica at 95°C.

sample with no halloysite the filler clay, had the slowest rate. Halloysite occurs as fine tubes less than 3µm long and about 0.2µm in diameter; it inherently has a higher surface area, a finer crystallite size and is normally less crystalline than the platy kaolinite. All of these features would make the halloysite more reactive than the kaolinite. The higher reactivity of halloysite compared to kaolinite has been noted previously in both caustic (Bell, 1970) and acidic (Deer, 1976) liquors. The reactive silica in the bauxite dissolved faster than the pure kaolins (Figure 9), but at a rate similar to the minesite kaolins. The kaolin in the Darling Range bauxite is predominantly fine halloysite, less than 1µm long and 0.05µm diameter (Anand and Gilkes, 1984). That halloysite is finer than in the D2 kaolin and thus a higher rate would be expected. No attempt was made to quantify the proportion of halloysite and kaolinite in the samples. To quantify the amounts by x-ray diffraction is extremely difficult in pure clays; for kaolin in bauxite it would be virtually impossible. Electron microscopy as a quantitative technique is both slow and prone to selectivity; for bauxites containing low levels of reactive silica it would not be feasible.

The platelets of kaolinite in the filler clay which made up the particles were about 0.5µm square and 0.1µm thick. Platelets of that size are equivalent to a surface area of about 10m²g⁻¹ which was the measured value. No major effect of particle size occurred; the slight decrease in rate at the coarser particle size was of a similar magnitude to the slight decrease in surface area. The lack of particle size effect suggests that the kaolin reacts both internally and externally, possibly utilising most of the available mineral surface area. Hence, in kaolins where only kaolinite is present, the crystallite size of the kaolinite is expected to determine the rate of reaction.

Effect of Digest Conditions

The dissolution reaction of kaolin in free caustic solutions was found to be controlled by the rate of chemical reaction at the mineral surface for the temperature range studied, 65 to 150°C. The activation energy of the reaction was 93kJmol⁻¹ for pure kaolin clay samples and 99kJmol⁻¹ for bauxite reactive silica. As the data for the pure kaolin was less variable, that activation energy is the preferred value.

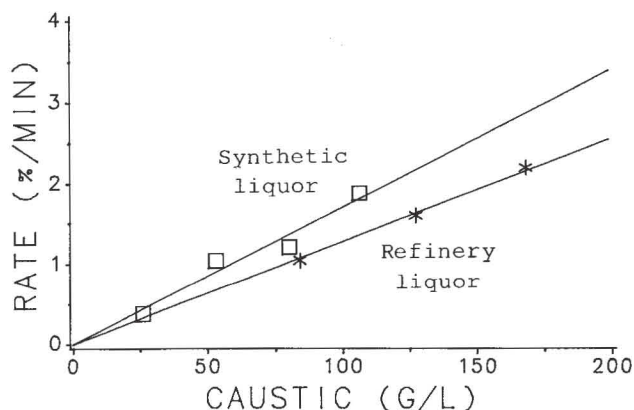


Figure 10 - Effect of free caustic on the rate for D2 kaolin in synthetic and refinery liquors.

For dissolutions of D2 kaolin in synthetic and refinery liquors, linear relationships between rate and free caustic concentration were found (Figure 10). The slopes of the lines are 1.75 for D2 kaolin in synthetic liquor (0gL⁻¹ Al₂O₃) and 1.25 for D2 kaolin in refinery liquor (57gL⁻¹ Al₂O₃). For dissolutions of D2 kaolin in synthetic liquor a marked effect of alumina on the rate was obtained. For dissolutions in refinery liquor there was little effect of alumina (Figure 11); in those dissolutions DSP precipitation occurred during dissolution. The precipitation of the DSP was directly observed by examining kaolin at 50% reacted (Figure 12). The typical "wool balls" of DSP are evident, about 1µm in size, residing on and between the sheets of kaolinite. If the correlation obtained with the refinery liquor data is extrapolated back to 0gL⁻¹ Al₂O₃, a rate similar to that for the equivalent free caustic concentration in synthetic liquor is obtained (broken line, Figure 11). That suggests that the DSP precipitation is not having an effect on the kaolin dissolution. Also, the effect of alumina concentration on the dissolution rate is quite different for the refinery and the synthetic liquors.

The reason for the less marked effect of alumina for refinery liquor digests may be associated with the formation of the DSP. With synthetic liquor, alumina and silica dissolve and are retained in solution; with refinery liquor there is little change in concentration of those species as they precipitate out. There may well be some form of interaction between the dissolution and precipitation reactions. Alternatively, the alumina in the refinery liquor may be in a different and more stable form (e.g. as aluminate dimers or complexed with silica or organics) than in the synthetic liquor; that might reduce the tendency for alumina to suppress the dissolution reaction. The silica solubility is very high in low alumina caustic liquors; the solubility decreases with increasing alumina concentration. However, above about 25gL⁻¹ Al₂O₃, the silica solubility increases with alumina concentration (Breuer et al, 1963). There may be some complex interactions between silica, alumina and DSP on the rate of dissolution with possibly different effects at high and low concentrations. The fortunate consequence is that in typical Bayer refinery liquors, with their high alumina concentration, the rate is essentially determined by the free caustic concentration. The dissolution rate will be slightly slower in green liquors than in spent liquors, primarily because of the lower free caustic concentration.

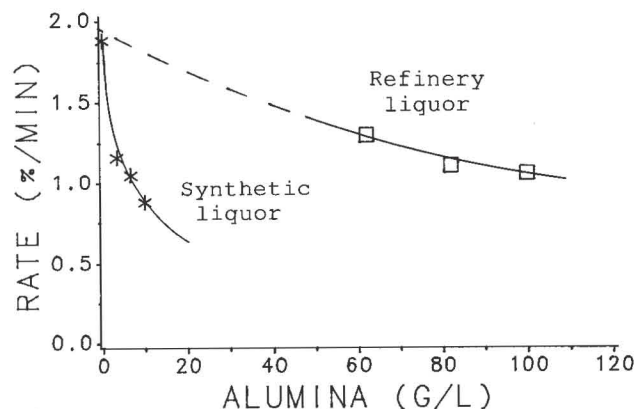


Figure 11 - The effect of alumina on the rate for D2 kaolin in synthetic and refinery liquors.

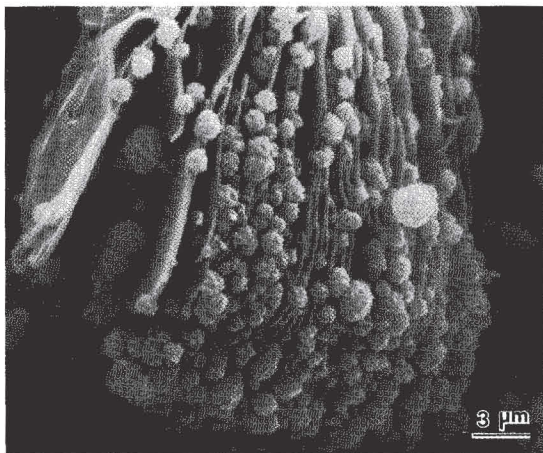


Figure 12 - Part reacted D2 kaolin in refinery liquor. The DSP 'wool balls' are apparent on and between the kaolinite plates.

Relevance To Bayer Refinery Desilication

In the Bayer process, the kaolin dissolution occurs in either the predigestion desilication tanks or the digesters. Alcoa of Australia Limited operates three refineries; two with and one without predigestion desilication. In the predigestion desilication tanks, it is essential to dissolve all the kaolin for optimum desilication. Typical operating conditions for such tanks are temperatures from 80 to 95°C and holding times from 6 to 12 hours. Those holding times are equal to that required for complete dissolution of the kaolin as determined in this work. Hence, factors which affect the kaolin dissolution rate can directly affect the desilication process in the refinery and the resulting level of silica in solution. In particular a major change in the type of kaolin in the bauxite, say from halloysite to kaolinite, could result in inadequate desilication. Although the normal reasons for poor desilication in such tanks are due to either too low an operating temperature or a reduced holding time, it is possible that a change in reactive silica mineralogy could be the cause. Such a change in mineralogy would necessitate a change in operating conditions.

For direct digestion of bauxite, typical operating conditions are 145°C and a residence time of thirty minutes. Even though the kaolin dissolution kinetics are much faster at such a temperature, kaolin dissolution would be only just complete. Hence the possibility exists of undigested kaolin occurring in refinery residue. Such undigested kaolin has been observed (Roach, 1983). It is the larger and more crystalline kaolinite particles, with their inherently slower dissolution kinetics, that remain undigested. Clearly the level of undigested kaolin will depend on both the reactive silica mineralogy and the operating conditions. Such undigested kaolin is beneficial, provided that adequate desilication occurs, as it represents a reduced fixed soda loss.

The kaolin dissolution data, when combined with similar kinetic data for the precipitation of DSP from liquor, enables a deterministic desilication model to be formed. Construction of such a model is, fortunately, not complicated by DSP precipitation affecting the rate of kaolin dissolution. Such a model can be used to predict the silica concentrations in liquor after digestion.

CONCLUSIONS

The mineralogy of the kaolin affects its dissolution rate in caustic liquors. Halloysite is more reactive than kaolinite. There is little effect of particle size on dissolution rate because of the porosity of the particles. The dissolution rate of kaolin in Bayer liquors is primarily determined by the free caustic concentration of the liquor. DSP precipitation does not affect the dissolution rate of kaolin. The dissolution rate of kaolin is sufficiently slow that it could affect the level of desilication achieved in predigestion desilication tanks and in digesters.

ACKNOWLEDGEMENTS

Several people have assisted in the production of the data; these include vacation students Stephen McGee and Teresa Alonso and colleagues David Del Pino and Ari Antonovsky (electron microscopy). We are grateful to Alcoa of Australia Limited for enabling us to pursue and publish this work.

REFERENCES

1. T. Oku and K. Yamada, "The Dissolution Rate of Quartz and the Rate of Desilication in the Bayer Liquor" (The Metallurgical Society of AIME), *Light Metals*, (1971) 31-45.
2. I.Z. Pevzner et al, "Mathematical Description of the Aluminate Solution Desiliconizing Process" *Tsvetnye Metally* 16(7)(1975), 53-57.
3. L.P. Ni et al, "Kinetics of the Desiliconising of Aluminate Solutions in Continuously Operating Reactors" *Soviet Non-Ferrous Metals Research* 6 (4) (1978), 155-157.
4. P.J. Cresswell, "Factors Affecting Desilication of Bayer Process Liquors". *Proc. XII Australian Chemical Engineering Conference*, 1984, 285-292.
5. D.K. Grubbs, "Reduction of Fixed Soda Loss in the Bayer Process by Low Temperature Processing of High Silica Bauxites" (The Metallurgical Society of AIME), *Light Metals*, (1987), 19-26.
6. G. Bell, "Alumina Losses in the Bayer Process. I: Behaviour of Silicate Minerals in Digestion" (Research Report, Aluminum Company of America, 1970).
7. W.A. Deer, R.A. Howie, J. Zussman, *Rock-Forming Minerals Vol. 3, Sheet Silicates*. (London: Longman Group Ltd., 1976.)
8. R.R. Anand and R.J. Gilkes, "Mineralogy of Darling Range Bauxite in Relation to Chemical Reactivity" (Western Australian Mining and Petroleum Research Institute, Project No 51, Report Dec. 1984).
9. G.I.D. Roach, "Gibbsite and Reactive Silica Analyses of Daily Plant Bauxite" (Internal Report, Alcoa of Australia Limited, 1983).