

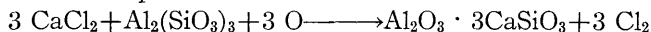
A STUDY OF THE REACTION BETWEEN OXYGEN AND MIXTURES OF KAOLINITE AND CERTAIN METAL CHLORIDES AT ELEVATED TEMPERATURES

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INTRODUCTION

The reaction between oxygen and mixtures of metal halides and kaolinite has been known for some time (Solvay, 1880, 1885, 1890; Kitaigorodskii *et al.*, 1935). Solvay found that when mixtures of calcium chloride and "siliceous clay-like substances" were reacted with air in a heated furnace, chlorine gas was produced. The reaction was pictured as follows:



Mixtures of sodium chloride and siliceous substances have been subjected to heat and electrolysis in the presence of oxygen. Such reactions have been reported to form alkali metal silicates and chlorine gas (Van Denburgh, 1901). Alkali aluminates together with hydrogen chloride and free chlorine have been produced by heating mixtures of alumina minerals, sodium chloride and carbon (or sulfur) in air containing sulfur dioxide and water vapor (Peniakoff, 1909). Since most of these reactions were carried out with the aim of producing hydrogen chloride, or chlorine, or both, very little work was done in establishing the identity of the solid silicate products. The author has examined some of these reactions with the purpose of determining the nature of the solid products.

MATERIALS AND PROCEDURES

A high grade Alabama kaolinite was used in all of the experiments described herein. An analysis of the kaolinite yielded 46.69 percent silicon dioxide (calculated for $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, 46.56%), 39.67 percent aluminum oxide (calculated value, 39.49%), and 12.60 percent water (calculated value, 13.93%). The kaolinite was ground to a fine powder in an agate mortar and that portion passing through a number 200 sieve was heated to a constant weight in a large platinum dish at a temperature of approximately 650°C. Heating separate samples of the kaolinite to a temperature of 900°C produced no further loss in weight; so, it was assumed that dehydration was complete at the lower temperature. It has been reported that the dehydration of kaolinite is practically complete at temperatures between 500 and 600°C (Eitel, 1954). The dehydrated material was stored in a stoppered bottle over anhydrous calcium sulfate in a desiccator. The nature and structure of the dehydrated kaolinite will be discussed at a later point in this paper.

Reagent grade sodium chloride, made by Baker and Adamson, was heated to a constant weight at 200°C. The salt was allowed to cool in a desiccator, then ground to a fine powder in an agate mortar. The salt was stored in the desiccator with the dehydrated kaolinite.

Reagent grade, anhydrous, calcium chloride, made by Baker and Adamson, was ground to a fine powder in an agate mortar and stored in a tightly stoppered bottle in a desiccator. Both the sodium chloride and calcium chloride were pulverized in a dry box to minimize hydration by exposure to the atmosphere.

The various mixtures of kaolinite, sodium chloride, and calcium chloride that were used in this investigation were prepared by placing the components (in the

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desired mole ratio) in tightly stoppered bottles and rolling and shaking each bottle for a period of 20 minutes to produce a homogeneous mixture. Precautions were taken during the weighing of the individual components to avoid hydration, and after the mixing operation, the bottles were placed in a desiccator.

All of the reactions between oxygen and the solid mixtures were carried out in a system consisting of 1. source of oxygen, 2. gas flow meter, 3. mercury safety valve, 4. ascarite tower, 5. alundum tube, extending through an electric tube furnace, 6. safety flask, and 7. chlorine absorption tower. "Tygon" tubing was used to connect all parts of the system. The alundum tube extended a sufficient distance beyond the furnace to prevent excessive heating of the "Tygon" tubing connections at each end. The oxygen used in the experiments was of U.S.P. grade. The chlorine absorption tower contained aqueous sodium hydroxide.

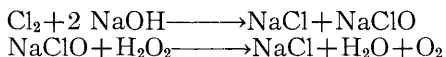
Generally speaking, the same procedure was followed in carrying out all of the reactions described herein.

1—A measured volume of sodium hydroxide solution was transferred to the absorption tower. A second and like volume of the base was placed in a titrating flask and used later as a blank.

2—A weighed sample of the solid mixture to be reacted was placed in an alundum boat, and the boat was pushed into the alundum tube to a point near the center of the furnace. Large alundum boats were used (13 x 2 x 1 cm.) and the solid was spread evenly over the bottom of the boat to afford a maximum surface area for reaction. The end of the boat facing the oncoming oxygen was cut down to allow a more even flow of the gas over the sample.

3—The system was closed; the rate of oxygen flow was adjusted; and the furnace was turned on with the rheostat at the proper setting. At the end of each trial run, the absorption tower was removed from the system and the flow of oxygen was stopped. After the sample and furnace had cooled to room temperature, the boat was removed and its solid contents were placed in a stoppered bottle for examination at a later time. Both ends of the furnace tube were plugged with ascarite tubes during the cooling period.

4—The sodium hydroxide solution in the absorption tower was treated with 15 ml. of 30 percent hydrogen peroxide and titrated with standard hydrochloric acid to a methyl orange-xylene cyanol end point. The sodium hydroxide blank was treated in a like manner.



The amount of chlorine liberated during the reaction and absorbed by the sodium hydroxide was calculated as follows:

$$[(\text{Vol. HCl (blank)} - \text{Vol. HCl (absorption tower)}) \times N \text{ (normality of HCl)}] \times 0.0355 = \text{weight of chlorine (grams)}$$

The electric tube furnace was calibrated with an iron-constantan thermocouple and the temperature of the furnace was plotted against time for various rheostat settings. It was noted that a period of about one hour was required before the furnace reached a maximum temperature at each rheostat setting. In all of the trial runs made, the warm up period of one hour was not considered in the total time that the sample was to be in the furnace at the given final temperature.

Certain of the reaction products were examined by x-ray diffraction methods. A General Electric Model XRD3 x-ray apparatus, with Cu K alpha radiation (nickel filter) and a camera of 14.32 cm. diameter was used. The samples were sealed in pyrex capillary tubes to prevent hydration during the analysis. Differential thermal analysis was employed in some cases for comparing the final products of the reaction with the reactants. The method and apparatus has been described and used previously for identifying various mineral products (Kalousek *et al.*, 1949).

RESULTS

Reaction between Oxygen and Mixtures of Kaolinite and Sodium Chloride

Two mixtures of kaolinite and sodium chloride were reacted with oxygen at elevated temperatures. The composition of the solid mixture prior to its reaction, the experimental conditions, and the amount of chlorine gas evolved during the reaction have been summarized in table 1. When portions of the sodium chloride, used in the preparation of the mixtures, were placed in the reaction chamber (trial # 6, table 1), there was no change noted in the concentration of the sodium hydroxide in the absorption tower.

TABLE 1

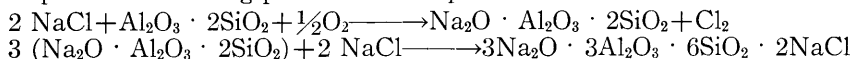
Reaction between oxygen and mixtures of kaolinite, sodium chloride, and calcium chloride at elevated temperatures

Trial	Composition of Solid Reactant ^a	Temp. °C	Time hr.	Per Cent of Total Chlorine in Reactant Liberated ^b
1.	Al ₂ O ₃ ·2SiO ₂ and NaCl in a 1:1 mole ratio, sample wt. = 1.000 g.	600	1	5.9
2.	Same as trial # 1	600	2	14.7
3.	Same as trial # 1	600	3	16.5
4.	Same as trial # 1	800	2	43.8
5.	Al ₂ O ₃ ·2SiO ₂ and NaCl in a 1:2 mole ratio, sample wt. = 1.000 g.	800	2	19.1
6.	NaCl, sample wt. = 1.000 g.	800	2	0.0
7.	Al ₂ O ₃ ·2SiO ₂ and CaCl ₂ in a 1:1 mole ratio, sample wt. = 2.500 g.	700	1¼	7.3
8.	Same as trial # 7	800	2½	25.5
9.	Same as trial # 7	800	3	35.1
10.	Al ₂ O ₃ ·2SiO ₂ and CaCl ₂ in a 1:2 mole ratio, sample wt. = 2.500 g.	800	2½	85.0
11.	Al ₂ O ₃ ·2SiO ₂ and CaCl ₂ in a 2:1 mole ratio, sample wt. = 2.500 g.	800	3	34.8
12.	CaCl ₂ , sample wt. = 2.500 g.	800	2	0.0
13.	Al ₂ O ₃ ·2SiO ₂ , NaCl, and CaCl ₂ in a 1:1:2 mole ratio, sample wt. = 1.000 g.	800	2	35.0
14.	Al ₂ O ₃ ·2SiO ₂ , NaCl, and CaCl ₂ in a 1:2:4 mole ratio, sample wt. = 1.000 g.	800	2	37.5
15.	Same as trial # 14	800	3	47.0
16.	Same as trial # 14	800	3½	52.0
17.	Same as trial # 14	800	9	97.7
18.	Same as trial # 14, but the Al ₂ O ₃ ·2SiO ₂ was pre-ignited to 1000°C	800	3	36.0

^aThe rate of oxygen flow through the system was approximately 4 liters per hour in all of the trials.

^bOnly the best of several determinations has been reported in this table.

The solid product of trial # 4 (table 1) was examined by x-ray diffraction methods and the measured "d" values have been listed in table 2. A comparison of these values with those of the other substances listed in table 2 indicates that some unreacted kaolinite as well as sodium chloride is present. There is little or no agreement between the x-ray data of the product and those reported for the various sodium aluminates and sodium silicates thus far prepared and identified by other workers (A.S.T.M., 1945). Although the x-ray data are not conclusive, there is evidence that nephelite, Na₂O·Al₂O₃·2SiO₂, and sodalite, 3Na₂O·3Al₂O₃·6SiO₂·2NaCl, are present in the reaction product. The formation of these products might be pictured as taking place in two steps.



According to these proposed reactions, a mixture of sodium chloride and kaolinite, in a 1:1 mole ratio, would liberate 75 per cent of the total chlorine present as chloride ion during the chemical change. Since the measured percentage of chlorine evolved in the best of several trials made is considerably lower than this theoretical value, and since unreacted kaolinite and sodium chloride are present in the product, it can only be concluded that the proposed reactions are not complete under the chosen experimental conditions.

Reaction between Oxygen and Mixtures of Kaolinite and Calcium Chloride

Three different mixtures of kaolinite and calcium chloride were reacted with oxygen. The composition of the mixtures, the experimental conditions, and the amount of chlorine gas produced by the reactions have been summarized in table 1. A portion of the calcium chloride used in the preparation of the mixtures was treated with oxygen at 800°C (trial # 12, table 1).

The x-ray diffraction data obtained for the product of trial # 10 (table 1) have been included in table 2. The data of table 2 indicate that both unreacted calcium chloride and kaolinite are present in the reaction product. There is good agreement between the measured "d" values of the product and those reported for calcium aluminum silicate, $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$. The x-ray data of the product show little or no agreement with those reported for various calcium aluminates and calcium silicates (A.S.T.M., 1945).

Reaction between Oxygen and Mixtures of Kaolinite, Sodium Chloride, and Calcium Chloride

Pertinent data concerning a few of the reactions carried out between oxygen and mixtures of kaolinite, sodium chloride, and calcium chloride have been summarized in table 1. A portion of the product of trial # 17 (table 1) was subjected to x-ray analysis. The x-ray data have been reported in table 2. Although calcium chloride and kaolinite appear to be absent in the product, there is evidence that some sodium chloride is still present. The measured "d" values of the product are in good agreement with those reported for calcium aluminum silicate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$. The fate of the reacted sodium chloride is unknown, although there is some indication that sodalite is present in the product. Some reacted calcium chloride has yet to be accounted for, since the compound identified is a 3:1 (CaO:kaolinite) combination while a 4:1 ratio was present in the original mixture. A survey of the x-ray data given in the literature (A.S.T.M., 1945) for various combinations of sodium oxide, calcium oxide, aluminum oxide, and silicon dioxide was made, but only the compound mentioned above seemed to agree with the x-ray data of the product.

Two of the reaction products (trials # 16 and # 17 in table 1) were examined by differential thermal analysis. The thermal analysis curves for these products along with those of the starting materials have been duplicated in figure 1. The curve for sodium chloride is fairly regular until its melting point is reached at 810°C. The curve for calcium chloride shows several endothermic peaks. Those peaks at 170 and at 200°C represent dehydration processes. The peak at 770°C corresponds with the melting point of the salt. In order to account for the dehydration peaks, it was assumed that the anhydrous material underwent some hydration during its preparation for thermal analysis and during the early stages of the analysis. The curve for the dehydrated kaolinite exhibits no endothermic or exothermic peaks over the temperature range of 20 to 800°C.

The thermal analysis curve of the product of trial # 16 has three pronounced endothermic peaks. The first, which occurs at 150°C, cannot be accounted for at this time. The minor peak at 190°C is probably due to the dehydration of unreacted calcium chloride in the product. The peak at 520°C seems to confirm this suspicion. The curve for the product of trial # 17 has only one pronounced

endothermic peak and that occurs at 150°C. This peak coincides with that of the other product. None of the calcium chloride peaks are evident in the curve; and its absence is in agreement with the x-ray data of table 2. The fact that the thermal analysis curves for both products show identical peaks at 150°C is a good indication that the same substance (or substances) is present.

Since the mixture of kaolinite, sodium chloride, and calcium chloride, in a 1:2:4 mole ratio, appeared to undergo considerable reaction with oxygen, attention was turned to the study of the kinetics of the reaction. Numerous experiments were carried out to determine the effect of the rate of flow of oxygen

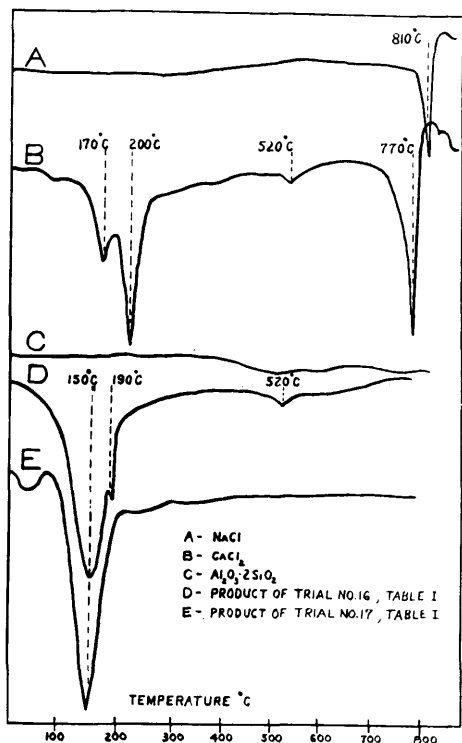


FIGURE 1

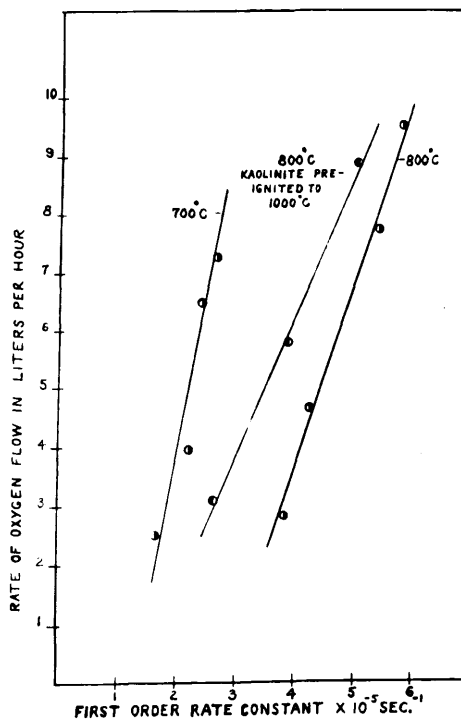


FIGURE 2

FIGURE 1. Differential Thermal Analysis Curves.

FIGURE 2. Relationship between reaction rate of oxygen with mixtures of kaolinite, calcium chloride and sodium chloride and the rate of oxygen flow through the reaction chamber.

through the reaction chamber on the extent and rate of the reaction. During each trial run the amount of chlorine liberated was determined at various time intervals. The results of a typical set of experiments have been summarized in table 3. The rate data in table 3 follow a first order pattern with respect to the chlorine present as chloride ion in the reaction mixture. The rate constants calculated from these and other data have been recorded in table 4.

Since the rate constants increase proportionally with an increase in rate of oxygen flow, it appears that the reaction is first order with respect to both the concentration of the halide ion and the amount of oxygen in the reaction chamber. The calculated rate constants have been plotted against rate of oxygen flow in

TABLE 2

X-ray diffraction data of reactants and products of the reaction between oxygen and mixtures of kaolinite, sodium chloride, and calcium chloride at elevated temperatures

Kaolinite (anhydrous)		Sodium Chloride		Calcium Chloride		Nephelite		Sodalite		CaO·Al ₂ O ₃ ·2SiO ₂		3CaO·Al ₂ O ₃ ·2SiO ₂		Reaction Products (table 1)		trial # 4		trial # 10		trial # 17			
d	I/I _o	d	I/I _o	d	I/I _o	d	I/I _o	d	I/I _o	d	I/I _o	d	I/I _o	d	I/I _o	d	I/I _o	d	I/I _o	d	I/I _o	d	I/I _o
				4.46	60			4.58	40	4.61	40									4.44	M		
						4.21	80			4.04	60			4.23	S			4.03	M	4.24	W		
						3.83	80			3.70	40			3.81	M			3.71	M	3.81	VW		
3.70	M							3.68	100	3.70	40			3.70	S					3.67	W		
										3.57	60												
3.51	MW			3.43	20			3.43	70					3.49	S					3.41	VW		
3.34	VS													3.35	VS	3.33	S			3.26	W		
		3.25	50			3.27	70	3.23	40			3.19	100	3.25	M								
				3.03	100	3.01	100			2.96	60	2.98	100			3.00	M	3.20	S				
																		2.95	M	2.98	S		
2.92	M							2.91	40									2.90	M				
				2.84	60	2.87	70	2.85	60					2.83	M			2.83	M	2.88	VW		
		2.81	100					2.79	60	2.79	60			2.75	M					2.81	VS		
2.64	M							2.69	40	2.65	40	2.67	100					2.62	M	2.66	S		
						2.56	60	2.60	90					2.60	M								
								2.50	40	2.51	70	2.53	40	2.52	VW			2.48	M	2.54	W		
								2.41	60					2.42	40	2.44	M						
														2.32	40					2.43	M		
				2.32	80	2.34	80													2.34	W		
						2.29	70							2.27	W								
2.23	MW			2.23	60			2.25	70					2.22	W	2.21	M						
2.11	MW							2.13	80	2.13	50	2.14	60	2.11	W	2.10	W	2.11	W	2.11	W		
				2.07	60	2.08	60			2.08	40					2.05	M						
		1.99	90			1.93	60	1.93	70	1.94	40			1.97	W					1.98	VS		
																				1.94	VW		
				1.90	80							1.92	60							1.91	W		
1.88	MW			1.85	60			1.83	40					1.88	W					1.84	M		

figure 2. Of course, there is always some question as to the validity of the rate constant calculated for a heterogeneous system, and one can only say that a reaction in such a system appears to be of a certain order.

Mixtures of the same ratio but containing kaolinite which had been pre-ignited to 1000°C were found to react somewhat slower with oxygen than those mixtures containing kaolinite which had been dehydrated at 650°C. Reactions between

TABLE 3

The effect of the rate of oxygen flow on the rate of the reaction between oxygen and mixtures of kaolinite, sodium chloride and calcium chloride (1:2:4 mole ratio) at 800°C

Time (minutes) ^a	Amount of Chlorine Gas Evolved ^b		
	Oxygen Flow 2.86 liter/hr.	Oxygen Flow 4.68 liter/hr.	Oxygen Flow 7.80 liter/hr.
60	0.0470 g.	0.0488 g.	0.0679 g.
90	0.0818	0.0958	0.1044
120	0.1088	0.1219	0.1375
150	0.1314	0.1463	0.1652
180		0.1689	
195			0.2052
210	0.1680		
240		0.2124	0.2400
275	0.2046		

^aTime zero was taken when the sample was placed in the furnace at room temperature and the flow of oxygen was started.

^bThe total amount of chlorine in each sample (as chloride) = 0.4500 g.

TABLE 4

First order rate constants for the reaction between oxygen and mixtures of kaolinite, sodium chloride, and calcium chloride

Solid Reactants	Temp. °C	Rate of Oxygen Flow (Liter/hr.)	First Order Rate Constant (Sec. ⁻¹)
Al ₂ O ₃ ·2SiO ₂ , NaCl, and CaCl ₂ in a 1:2:4 mole ratio	700	2.53	1.7 ± 0.2 × 10 ⁻⁵
	700	3.98	2.2 ± 0.1 × 10 ⁻⁵
	700	6.50	2.4 ± 0.1 × 10 ⁻⁵
	700	7.20	2.7 ± 0.3 × 10 ⁻⁵
	800	2.86	3.8 ± 0.3 × 10 ⁻⁵
	800	4.68	4.3 ± 0.1 × 10 ⁻⁵
	800	7.80	5.5 ± 0.1 × 10 ⁻⁵
	800	9.60	5.9 ± 0.2 × 10 ⁻⁵
	Same mixture as that described above, but the kaolinite was pre ignited to 1000°C	800	3.10
800		5.80	3.9 ± 0.2 × 10 ⁻⁵
800		8.92	5.1 ± 0.1 × 10 ⁻⁵

oxygen and mixtures of the same composition but containing hydrated kaolinite were also examined. The rate constants calculated for these reactions (at 800°C and with various rates of oxygen flow) were not as consistent as those obtained with the pre-ignited kaolinite. The reaction was observed to be very slow in its initial stages, but as it proceeded, its rate gradually approached that measured for the anhydrous kaolinite. The slow initial rate can be attributed to competi-

tion between oxygen trying to approach the solid mixture and the water vapor being driven out of the solid. As dehydration subsides, it is reasonable to assume that the rate of reaction would approach that previously noted for anhydrous kaolinite.

DISCUSSION OF RESULTS

The dehydration of kaolinite has been the topic of numerous investigations (Eitel, 1954). It has been observed that the dehydration sets in at about 450°C and that meta-kaolinite is formed at temperatures within the range of 480 to 650°C. The crystal structure and the particle size of the kaolinite play an important part in determining the temperature at which this process begins and ends. Meta-kaolinite has also been the subject of considerable study. It has been reported to be homogeneous, like the individual crystal of kaolinite, and is often considered to be an unstable semi-crystalline complex. The readiness with which it reacts with acids and bases, in direct contrast to the behavior of hydrated kaolinite, seems to agree with this concept. When meta-kaolinite is heated above 900°C, it disintegrates to form a mixture of silica and alumina, and at temperatures above 1000°C fine mullite needles, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, have been observed (Eitel, 1954).

The difference between the reactivity of the mixtures containing kaolinite which had been pre-ignited to 1000°C and those in which the kaolinite had been pre-ignited to 650°C (table 1 and 4) can be accounted for on the basis of the structure of the pre-ignited kaolinite, itself. The former is either a mixture of oxides or an aluminum silicate (in the case of mullite) which is resistant to chemical attack, while the latter is a "loose" crystalline structure, quite susceptible to the chemical action of alkaline oxides.

Both sodium chloride and calcium chloride failed to react with oxygen in the absence of kaolinite (table 1). This would seem to indicate that the kaolinite not only acts as an acceptor for the oxides of sodium and calcium, once they have been formed, but that it also serves as a catalyst in the replacement of the chloride ion with the oxide ion in the sodium and calcium chlorides.

The production of nephelite (or nepheline) by the reaction of oxygen with mixtures of kaolinite and sodium chloride does not represent a new synthesis. Nephelite has been recently synthesized by heating mixtures of sodium carbonate, aluminum oxide, and silicon dioxide to 1200°C (Miyashiro *et al.*, 1954).

LITERATURE CITED

- American Society for Testing Materials (A.S.T.M.). 1945. Alphabetical Index of X-Ray Diffraction Patterns, Philadelphia.
- Eitel, W. 1954. The Physical Chemistry of the Silicates. The University of Chicago Press, Chicago.
- Kalousek, G. L., C. W. Davis, Jr. and W. E. Schmertz. 1949. Investigation of hydrating cements and related hydrous solids by differential thermal analysis. J. Am. Concrete Inst. 20: 693-712.
- Kitaigorodskii, I. I and V. I. Bokunyawa. 1935. The interaction of sodium chloride and kaolin at high temperatures. J. Applied Chem. (USSR) 8: 230-237.
- Miyashiro, A. and T. Miyashiro. 1954. Unit cell dimensions of Synthetic nepheline. J. Fac. Sci. Univ. Tokyo, Sect. II. 9: 267-270.
- Peniakoff, S. A. 1909. Continuous Production of Alkali Aluminate and Alkali Chlorides, Together with Hydrochloric Acid and Free Chlorine. French Patent No. 420,461, November 24.
- Solvay, E. 1880. Apparatus for the Decomposition of Chloride of Calcium. United States Patent No. 235,820, December 21.
- . 1885. Manufacture of Chlorine. United States Patent No. 316,195, April 21.
- . 1890. Process of Making Chlorine. United States Patent No. 420,837, February 4.
- Van Denburgh, F. P. 1901. Process for the Manufacturing of Silicates. United States Patent No. 677,906, July 9.