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From: Chief, Naval Technical Mission to Japan.
To : Chief of Naval Operations.
Subject: Target Report - Japanese Metallurgy, Recovery of
Aluminum from Clay and Shale.
Reference: (a) "Intelligence Targets Japan" (DNI) of 4 Sept. 1945.

1. Article 2 of the report outlined by Target X-13 of Fascicle X-1 of reference (a), covering the subject of recovery of aluminum from clay and shale, is submitted herewith.

2. The report was prepared by Lieut. J.H. Norwood, USNR, assisted by Capt. Milton S. Zaslow, AUS, as interpreter and translator.



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RESTRICTED

X-13-2

**JAPANESE METALLURGY - ARTICLE 2
RECOVERY OF ALUMINUM FROM CLAY AND SHALE**

**"INTELLIGENCE TARGETS JAPAN" (DNI) OF 4 SEPT. 1945
FASCICLE X-1, TARGET X-13, ARTICLE 2**

NOVEMBER 1945

U.S. NAVAL TECHNICAL MISSION TO JAPAN

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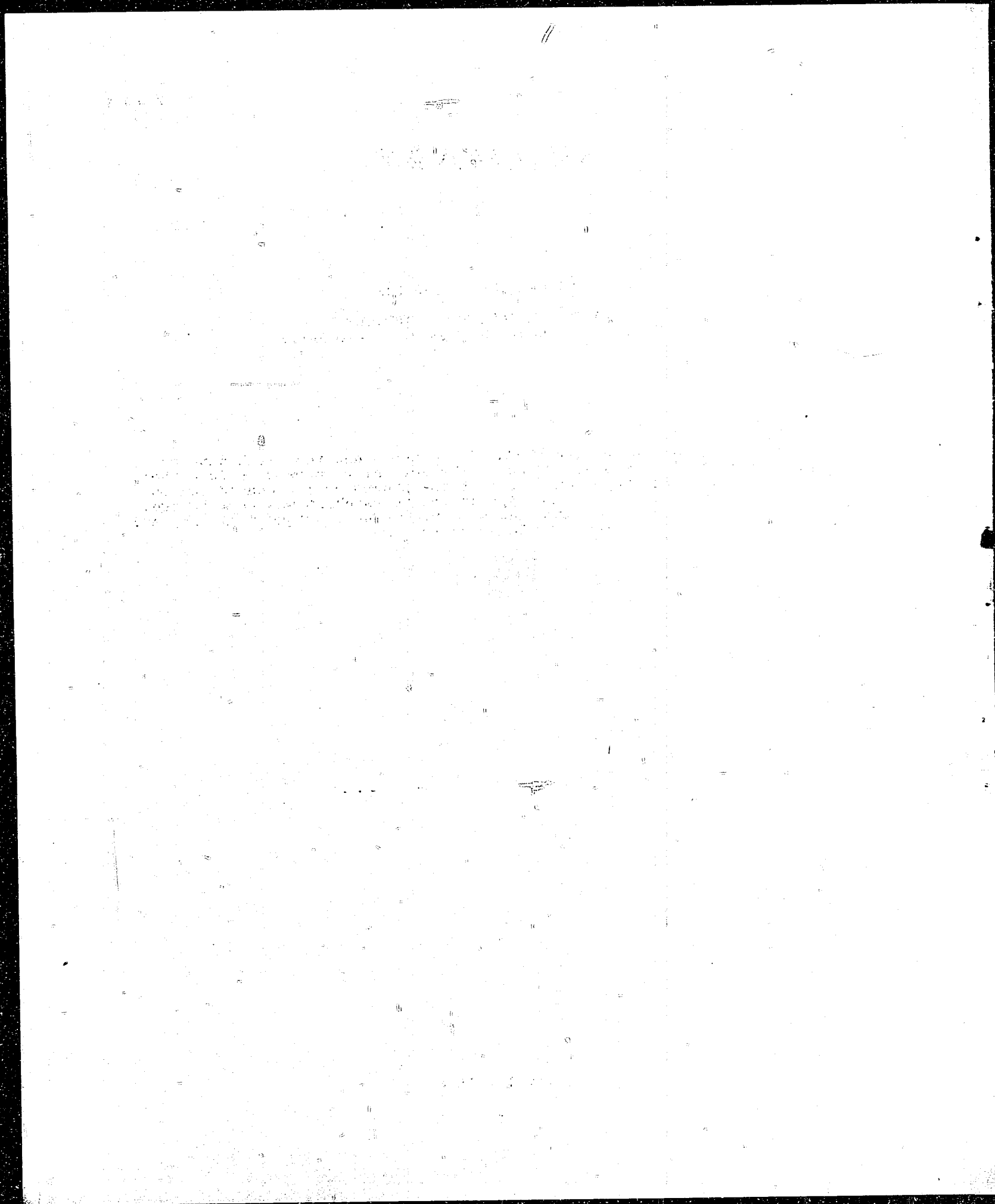
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SUMMARY

MISCELLANEOUS TARGETS

JAPANESE METALLURGY - ARTICLE 2 RECOVERY OF ALUMINUM FROM CLAY AND SHALE

This report deals with production methods and technical data on "Aluminum from Clay and Shale." Each of the several processes is described and the yield from each reported. None of the processes was considered outstanding. Each was applied to the type of ore to which it was best suited. The economic and technical disadvantages of producing aluminum from clay and shale were by no means overcome by Japanese research.



REFERENCES

Location of Target:

Institute for Light Metals, TOKYO.

Non-Ferrous Metals Division, Department of Patents and Standards,
Navy Technical Department (Air).

Names of Japanese Personnel Who Assisted in Gathering Documents:

Rear Adm. Yoshio KUBOTA, IJN, Head, Navy Technical Department (Air).

Lt. Comdr. I. HIRAOKA, Light Metals Bureau.

Names of Japanese Personnel Interviewed:

T. OKUYAMA and E. KATAYAMA, Civilian engineers, Aluminum Section,
Non-Ferrous Metals Division, Department of Patents and Standards;
both capable technicians of 'over 15 years' experience.

LIST OF ENCLOSURES

(A) Production Figures 1945 - By Plant and Type of Process.

INTRODUCTION

Cut off from the bauxite necessary to conventional aluminum production, the Japanese were forced to use low-quality ores such as shales and clay as a source of aluminum oxide. The reduction of these ores is an expensive process and the resulting product is highly impure (Fe-Si). None of the processes described here was considered a technical success by the Japanese and all operated at a considerable economic disadvantage.

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THE REPORT

PART I - PROCESSES

1. The various processes, in use and under development, for obtaining alumina from low grade ores are shown in Table I.

TABLE I
ALUMINA FROM ALUMINOUS SHALE, ALUNITE AND CLAY

<u>Ore Type</u>	<u>Process</u>
Aluminous shale	a. Soda-lime process
	b. Direct process (conc. caustic soda)
	c. Semi-fused process
	d. Direct electrolytic process
	e. Dry method
Alunite	a. Caustic soda process
	b. Magnesite process
	c. Milk of Magnesia process
	d. Ammonia process
Clay (including phosphatic clay)	a. Sulfuric acid process
	b. Sulfurous acid process
	c. Hydrochloric acid process
	d. Calcium sulphate process

2. The processes for obtaining alumina from aluminous shale are described in detail as follows:

a. Soda-lime process

Aluminous shale is sintered in a rotary kiln with soda-ash and lime-stone at about 1200°C. as in the case of cement manufacture. The sintered clinker is pulverized and treated with hot dilute solution of sodium carbonate for 15 minutes to make up the sodium aluminate solution from which the residue is separated. Then the aluminate solution is desilicated in the autoclave at 150°C. for one hour, and goes to the BAYER process.

b. Direct process with concentrated caustic soda

Aluminous shale is digested with a highly concentrated solution of caustic soda at 160°C. for three hours, converting alumina to soluble sodium aluminate. The solution is then treated by the BAYER process.

c. Semi-fused process

The mixture of aluminous shale and caustic soda solution is heated in the rotary kiln at about 500°C. and the semi-fused product is digested with a concentrated solution of sodium aluminate at 160°C. for three hours. The aluminate solution is then treated by the BAYER process.

d. Direct electrolytic process

The electrolysing operation is carried on almost the same way as in the case of alumina. The molten metals, upon being tapped up from the bath, are immediately poured into cold water. Thus is obtained the hollow pebble-like mass of metal which may easily be attached by the alkali solution. The hollow pebble is dissolved with sodium aluminate solution and filtered off. The filtrate has large amounts of silica, hence the autoclave treatment must necessarily follow.

3. The processes used on alunite ore are described in detail below:

a. Caustic soda process

The dried ore is mixed with circulating caustic soda-sodium aluminate solution. The sludge is digested by steam at about 80°C. for three hours under constant agitation. The major portion of sulphate in the ore is taken out and converted to sodium sulphate. The sludge goes to the thickener where the residue is separated. The cake is mixed with a higher concentrated sodium aluminate solution and heated to about 90°C. for three hours. The sludge is brought into the thickener. From there it goes through the BAYER process.

b. Magnesite process

When a mixture of alunite and magnesite is heated at about 700°C. the sulphate part of the former can be combined with magnesia from the latter to form readily soluble magnesium sulphate. By washing the clinker with water to remove $MgSO_4$, the aluminous product which contains alkali soluble alumina is separated. The aluminous product is then treated by the BAYER process.

c. Milk of magnesia process

In this process, the ore alone may be roasted at a somewhat lower temperature (about 600°C.) merely to loosen the construction of alunite. The roasted alunite and the milk of magnesia are heated to 80°C. by steam and kept at this temperature for four hours under constant agitation. The mixture is then passed through the thickener and filtered off. The residue is then treated by the BAYER process.

d. Ammonia process

After the alunite is roasted at a temperature of 550-600°C. in a rotary kiln, it is treated with ammonium solution at 85°C. for 15 minutes. These muddy products are sedimented and counter-washed by the thickener. The upper pure solution is condensed in an effect evaporator and potassium ammonium sulphate crystals are produced. The sediment from the thickener is filtered and dried and then treated by the BAYER process.

4. The methods for obtaining alumina from clay are described in detail below:

a. Sulfuric acid process

After the ore is roasted in a rotary kiln at about 300°C., it is treated with sulfuric acid. The temperature rises to about 150°C. during one and a half hours, the mixture swells its volume and assumes a porous state. Reaction products are mixed with mother liquors into a solution, which contains ammonium alum, phosphoric solution and non-reacted materials. Separate cakes are formed in a filter press. On cooling the solution by air, ammonium alum crystallizes and is separated from the phosphoric solution. $Al(OH)_3$ and ammonium sulphate solution are obtained from alum by adding ammonium solution.

b. Sulfurous acid process

After the ore is roasted in a rotary kiln at about 600°C., it is digested with sulfurous acid solution. The alumina in the clay becomes aluminum sulfite solution. The reaction mixture is then passed through the thickener and separated from the silica. When the solution is heated to 100°C. by steam, aluminum sulfite is converted into basic aluminum sulfite. The cakes of this material are treated with caustic soda solution and aluminum hydroxide thus obtained. Sodium sulfite is treated with slaked lime to recover the caustic soda.

c. Hydrochloric acid process

The clay is dissolved with hydrochloric acid at a temperature of 125°C. by 2 kg. 1 cm.² pressure. The time required is two hours. Vacuum filters are used to filter and wash out silica. The filtered liquor was concentrated until small crystals of aluminum chloride (hydrated) grow. After the above is separated, it is calcined into alumina, recovering hydrochloric acid.

d. Calcium sulfate process

The clay is digested with dilute sulfuric acid at a temperature of about 100°C. for two hours, and the alumina in the clay is extracted as aluminum sulfate solution, which is separated from the insoluble residue. The aluminum sulfate solution, thus obtained, is neutralized with milk of lime at room temperature (slowly), and then aluminum hydroxide and calcium sulfate are precipitated as a mud. The mud is treated by oil flotation, and the crude aluminum hydroxide is separated leaving the calcium sulfate. This crude hydroxide is treated as bauxite in the BAYER process.

5. Raw materials are located as follows:

Aluminous shale	North CHINA
Alunite	IZU, SHIZUOKA Prefecture, JAPAN
Clay	KUROSAWAZIRI, IWATE Prefecture, JAPAN
	NAEKI, Gifu Prefecture, JAPAN
	MIE, OITA Prefecture, JAPAN
Phosphatic clay	KITA DAITO Jima, OKINAWA Prefecture

6. Chemical analysis of raw materials is shown in Table II.

TABLE II
CHEMICAL ANALYSIS OF RAW MATERIALS

Type Ore	I.L.*	H ₂ O	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	Misc.
Aluminous Shale	13.61	1.31	12.97	59.56	9.34	2.40			
	13.46	1.16	22.24	52.74	7.36	2.40			
Alunite	34.7		8.9	42.1			3.65	2.82	T.SO ₃ 31.2
	12.37		16.80	32.40			3.55	2.79	T.SO ₃ 29.97
Clay(IWATE) (GIFU) (OITA)	9.53		42.96	35.09	7.43				
	13		46	36	5				
	8.73		41.94	28.55	9.10				MgO 1.75
Phosphatic Clay	19.44	24.02	17.82	42.11	3.66				CaO 9.82 P ₂ O ₅ 25.90

*I.L. - ignition loss

PART II - PRODUCTS

1. The product desired from these processes was pure alumina (Al₂O₃) for reduction to aluminum for electrolytic refining. However, all of these processes produced a highly impure type of alumina as is shown by Table III.

TABLE III
CHEMICAL ANALYSIS OF ALUMINA OBTAINED

Process	I.L.*	Al ₂ O ₃	Na ₂ O	SO ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	Misc.
Soda-lime	1.49	95.36	2.69	0.16	0.20	0.10		
Direct	1.49	95.36	2.69	0.16	0.20	0.10		
Semi-fused	1.49	95.36	2.69	0.16	0.20	0.10		
Direct-electrolytic	1.49	95.36	2.69	0.16	0.20	0.10		
Caustic soda	1.55	97.47			0.11	0.80	0.01	
Magnesite	1.55	97.47			0.11	0.80	0.01	
Milk of magnesite	1.55	97.47			0.11	0.80	0.01	
Ammonia (crude)		56.70	0.74	10.16	29.40			K ₂ O 0.93 CaO 0.75 SO ₄ 0.06
Sulphuric acid	0.74	98.95			0.10	0.07		
Sulphurous acid		93.0			4.2	2.6		
Hydrochloric acid	7.0	90.3			0.5	1.2		Cl 1.0
Calcium sulphate		97.20	trace	trace	0.12	0.35	trace	
Calcium (crude)		52.21		11.32	3.80	12.98	1.21	CaO 1.94

*I.L. - ignition loss

2. Naturally from such an impure alumina a high purity aluminum could not be obtained as is shown in Table IV.

TABLE IV
CHEMICAL ANALYSIS OF FINISHED PRODUCT

Process	Al	Fe	Si
Calcium sulphate	98.26	0.78	0.96
Soda-lime	99.01	0.61	0.38
Direct electrolytic	79.78	10.84	9.38

3. The yield of Al₂O₃ is not high as is shown by Table V.

TABLE V
TONS OF ORE PER TON Al_2O_3 DERIVED

Process	Ore Type			
	Shale	Alunite	Clay	Phosphatic Clay
Soda lime	7.0			
Direct	6.0			
Semi-fused	5.5			
Direct electrolytic	4.5			
Caustic soda		5.0		
Magnesite		5.0		
Milk of Magnesia		5.0		
Ammonia		4.5		
Sulphuric acid				10.0
Sulphurous acid			11.0	
Hydrochloric acid			3.5	
Calcium sulphate			11.0	

4. In addition the cost is high as shown in Table VI.

TABLE VI
COST - YEN PER METRIC TON

Process	Al_2O_3	Al
BAYER Process (bauxite)	360	1,900
Soda-lime Process	1,350	3,970
Dry Process	850	2,840
Caustic soda Process	2,400	---
Sulphuric acid Process	2,500	---

5. Production figures for 1945 are shown in Enclosure (A).
6. To summarize, production of aluminum from clay and shale in JAPAN was strictly a war-time measure. None of the processes was considered a technical success due to the high percentage of impurities and none was economically feasible. The Japanese were able to develop no process which can compete at present with the conventional BAYER process for producing aluminum from bauxite.

ENCLOSURE (A)

MONTHLY ALUMINA PRODUCTION IN 1945											
No.	Name of Company	Name of Factory	Materials	Method	Production in metric tons						Total
					Jan.	Feb.	March	April	May	June	
1.	Nippon Soda Co. Ltd.	Takaoka Factory	Bauxite	Bayer method	628	234	231	103	426	587	2245
			Aluminous Shale	Semi-fused method							
2.	Nippon Keikinzoku Co. Ltd.	Shimizu Factory	Bauxite	Bayer method							
			Aluminous Shale	Soda-lime method	2024	3080	2345	1724	1468	362	11,003
			Alunite	Mix of magnesite method							
3.	Nippon Aluminium Co. Ltd.	Kurasaki Factory	Aluminous Shale	Soda-lime method	135	192	360	376	540	145	1748
4.	Showa Denko Co. Ltd.	Yokohama Factory	Bauxite	Bayer method	1460	1284	1867	805	915	536	6867
			Aluminous Shale	Direct method							
5.	Sumitomo Kagaku Kogyu Co. Ltd.	Niihama Factory	Bauxite	Bayer method							
			Aluminous Shale	Soda-lime/Semi-fused	587	425	496	709	520	433	3170
				Direct-method							
6.	Mitsui Keikinzoku Co. Ltd.	Miike Factory	Aluminous Shale	Soda-lime method	124	32	146	165	191	57	715
7.	Nitto Kagaku Kogyu Co. Ltd.	Hachinohe Factory	Clay	Sulfuric acid method	38	0	46	4	0	15	103
8.	Kokusen Keigin Kogyo Co. Ltd.	Iwate Factory	Clay	Sulfurous acid method	0	0	12	15	40	33	100
9.	Asada Kagaku Kogyu Co. Ltd.	Shikama Factory	Alunite	Caustic-soda method	54	30	0	74	54	21	233
10.	Showa Denko Co. Ltd.	Toyama	Aluminous Shale	Dry method	726	729	810	753	817	746	4581
11.	Toyo Soda Kogyo Co. Ltd.	Tanda Factory	Aluminous Shale	Soda-lime method	175	304	194	502	487	784	2447
12.	Showa Denko Co. Ltd.	Kanose Factory	Aluminous Shale	Dry method	-	-	-	-	-	-	-
13.	Dai Nippon Kagaku Kogyo Co. Ltd.	Kawasaki Factory	Clay	Hydrochloric acid method	21	23	2	2	0	0	48
		Total of Inland			5973	6333	6509	5232	5494	3719	33260
14.	Nippon Chisso Hiryo Co. Ltd.	Konan Factory	Aluminous Shale	Soda-lime method	241	334	399	404	331	282	1991
15.	Chosen Keikinzoku Co. Ltd.	Chinampo Factory	Aluminous Shale	Dry method	322	341	354	295	276	222	1810
		Total of Korea			563	675	753	699	607	504	3801
16.	Nippon Aluminium Co. Ltd.	Takao Factory	Bauxite	Bayer method	733	282	-	-	-	-	1015
		Total of Formosa			733	282	-	-	-	-	1015
		Total of Japan			7269	7290	7262	5931	6101	4223	36076