GM 14447

REPORT ON PREPARATION OF NbCl5 FROM ORE CONCENTRATES (INVESTIGATION REPORT IR 60-123)

Lac des 2 Montagnes Twp

INDUSTRIAL CONFIDENTIAL

CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 60-123

THE PREPARATION OF $NbCl_5$ FROM ORE CONCENTRATES OF COLUMBIUM MINING PRODUCTS LIMITED, OKA, QUE.

Ministère des Richesses Naturelles, Québec

SERVICE DES GITES MINÉRAUX

No GM- 14447

by

B. J. P. WHALLEY, T. R. INGRAHAM AND P. MARIER

EXTRACTION METALLURGY DIVISION

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COPY NO. 7

DECEMBER 15, 1960

Industrial Confidential

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THE PREPARATION OF $NbCl_5$ FROM ORE CONCENTRATES OF COLUMBIUM MINING PRODUCTS LIMITED, OKA, QUE.

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B. J. P. Whalley[*], T.R. Ingraham[**] and P. Marier[***]

SUMMARY OF RESULTS

A niobium concentrate containing about 25 per cent Nb_2O_5 was chlorinated with chlorine in the presence of carbon. Because of the nature of the mineralization, the chlorides of niobium, calcium, iron, magnesium, titanium, aluminum and other metals were formed. In the initial separation, the calcium, magnesium and other non-volatile chlorides remained with the chlorination residue. Aluminum and ferric ~~titanium~~ chlorides were separated in a low-melting sodium chloride eutectic. The remaining chlorides, all except niobium pentachloride and niobium oxychloride, were separated by selective condensation. The niobium oxychloride was converted with additional carbon and chlorine to niobium pentachloride. Niobium pentachloride can be cast readily for shipping or storage. In this form, with a small surface to volume ratio, it is stable if protected from moisture.

Niobium metal, virtually free of other metallic contaminants, was prepared by hydrogen reduction of the niobium pentachloride, thus showing that the concentrate could be used as a suitable source of niobium for the production of pure metal.

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[*] Senior Scientific Officer, [**] Head, Research Subdivision and [***] Scientific Officer, Extraction Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

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INTRODUCTION

Columbium Mining Products Limited at Oka, Quebec controls a substantial deposit of ore containing fractional percentages of niobium minerals. Largely through the work of the company's consulting engineer, Mr. H. L. Noblitt, the company has developed a beneficiation process for upgrading their ore. This process has been tested, at various stages in its development, in the Mines Branch Laboratories, and it has been demonstrated that concentrates containing up to 25 per cent Nb_2O_5 can be prepared.

Since there is a good possibility that, during the later stages of utilization of this ore body, the company may wish to diversify its activities by marketing more niobium products than just a variety of ore concentrates, the advice of the Mines Branch was sought on the preparation of other niobium compounds.

In conversations with Dr. K. W. Downes, Chief of the Extraction Metallurgy Division, the objectives of the company were explained by Mr. E. P. McDonough and Mr. H. L. Noblitt. It was observed that preliminary work done on the ore concentrates by Battelle Memorial Institute of Columbus, Ohio, U. S. A. had shown that selective hydrolysis, when combined with sulphuric acid leaching, could be used to prepare a chemical concentrate of niobium oxide. This work was of interest, and plans were made to develop the technique of selective hydrolysis still further at the Mines Branch.

This work is in progress and will be reported under other auspices at a later date.

Preliminary experiments done at Battelle Memorial Institute had shown that the concentrate was amenable to chlorination. Since the highest quality refractory metals are frequently produced via a halogen route, it was agreed that further studies should be made on the concentrate to determine whether niobium pentachloride could be produced from it without excessively large chlorine losses to gangue constituents.

A preliminary report on the results of some of this work was made in Extraction Metallurgy Division Internal Report EMT 60-3, January 26, 1960.

In this investigation report, experiments done to chlorinate the concentrate will be described. Methods used to recover a pure niobium pentachloride from the mixed chlorides will be discussed, and metal prepared from the pentachloride will be compared with commercially acceptable metal.

ORE AND CHEMICALS

Mineralogy

Two niobium minerals have been reported (1, 2) in the Columbium Mining Products Limited ore, pyrochlore and perovskite.

The pyrochlore mineral is the more abundant and contains sodium, calcium, niobium, oxygen and fluorine. The perovskite mineral, which normally contains only calcium, titanium and oxygen, in this occurrence has about one-quarter of the titanium substituted by niobium. Grain sizes of the various minerals indicate that over 90 per cent liberation could be achieved at -200 mesh.

Analysis of Concentrate

The concentrate provided by Mr. H. L. Noblitt for this work contained:

Nb_2O_5	24.7%	Rare Earths and ThO_2	5.1%
CaO	17.6%	ZrO_2	1.1%
SiO_2	14.1%	BaO	trace
Fe_2O_3	12.3%	SrO	0.26%
MgO	7.5%	Y_2O_3	0.04%
TiO_2	6.3%	V_2O_5	0.05%
Al_2O_3	3.1%		

Quality of Chemicals Used

Cylinder grade chlorine, as supplied by Canadian Industries Limited was used. The carbon used in the reaction was either ground graphite or steam activated cocoanut shell charcoal. The sodium chloride used was coarsely crystalline reagent grade material.

METALLURGICAL ASSESSMENT

In the chlorination of oxide minerals of the types present in this concentrate, the principal chlorination reaction can be written:

$$MO + Cl_2 = MCl_2 + 1/2\,O_2 \qquad \ldots\ldots\ldots\ldots\ldots 1.$$

When the free energies of the various constituents are substituted in this equation, it can be presumed that the reaction is likely to proceed as written if the free energy change is negative. This free energy change is negative only for the chlorination of relatively few of the oxides in the minerals. To make the chlorination reactions for the remaining oxides proceed, it is necessary to reduce the oxygen pressure in the system by the addition of some reagent such as carbon or carbon monoxide.

$$C + 1/2\,O_2 = CO \qquad \ldots\ldots\ldots\ldots\ldots 2.$$

$$CO + 1/2\,O_2 = CO_2 \qquad \ldots\ldots\ldots\ldots\ldots 3.$$

If sufficient strong reducing agent is added, then it becomes theoretically possible to chlorinate all of the constituents.

It was of interest in this assessment to estimate the likelihood of chlorinating only a favoured few of the constituents of the ore. The estimate was made on the assumption that to a first approximation, the activity coefficients of the various oxides in the minerals are about the same, and hence their relative order of stability to chlorination would be the same as that of the pure oxides. The chlorination reactions, based on one mole of chlorine, were then written for all of the elements which might consume appreciable amounts of chlorine.

The reactions and the corresponding free energy changes (3, 4, 5) are as follows:

$Na_2O + Cl_2 \rightleftharpoons 2NaCl + 1/2\ O_2$ $\Delta F^\circ_{800^\circ C} = -37$ kcal....4.

$CaO + Cl_2 \rightleftharpoons CaCl_2 + 1/2\ O_2$ $\Delta F^\circ_{800^\circ C} = -32$ kcal....5.

$1/3Fe_2O_3 + Cl_2 \rightleftharpoons 1/3Fe_2Cl_6 + 1/2\ O_2$ $\Delta F^\circ_{800^\circ C} = -\ 7$ kcal....6.

$MgO + Cl_2 \rightleftharpoons MgCl_2 + 1/2\ O_2$ $\Delta F^\circ_{800^\circ C} = +\ 3$ kcal....7.

$1/3Nb_2O_5 + Cl_2 \rightleftharpoons 2/3NbOCl_3 + 1/2\ O_2$ $\Delta F^\circ_{800^\circ C} = +14$ kcal....8.

$1/2TiO_2 + Cl_2 \rightleftharpoons 1/2TiCl_4 + 1/2\ O_2$ $\Delta F^\circ_{800^\circ C} = +19$ kcal....9.

$1/3Al_2O_3 + Cl_2 \rightleftharpoons 1/3Al_2Cl_6 + 1/2\ O_2$ $\Delta F^\circ_{800^\circ C} = +23$ kcal...10.

$1/5Nb_2O_5 + Cl_2 \rightleftharpoons 2/5NbCl_5 + 1/2\ O_2$ $\Delta F^\circ_{800^\circ C} = +24$ kcal...11.

$1/2SiO_2 + Cl_2 \rightleftharpoons 1/2SiCl_4 + 1/2\ O_2$ $\Delta F^\circ_{800^\circ C} = +29$ kcal...12.

In the above series of reactions, the negative free energies for reactions 4, 5 and 6 indicate the probability that very little if any reducing agent would be required to bring about substantially complete chlorination of the elements sodium, calcium and iron.

The magnitude of the free energies for the remaining reactions suggest that if niobium pentachloride were produced directly as the sole niobium product, the severity of the reaction conditions required to produce it would probably be sufficient to cause the chlorination of all the constituents of the ore, with the possible exception of the silicon.

From the equations, there was an indication that if the reducing conditions could be adjusted to produce niobium oxychloride as the principal product, it might be possible to reduce the chlorine consumption by the amount required to chlorinate the titanium, aluminum and the silicon. It was visualized that the niobium oxychloride would be rechlorinated in a separate stage to produce niobium pentachloride.

Thermodynamic calculations of the degree of precise control of the CO/CO_2 ratio required to chlorinate the niobium, but to prevent the chlorination of the titanium, aluminum and silicon were not encouraging. The amount of control required seemed to be greater than that which might be conveniently exerted on the reaction. Hence it was decided that no attempt should be made to seek selectivity of the chlorination reactions on the basis of thermodynamic considerations. Instead, it was decided to determine the optimum reaction conditions for producing niobium pentachloride and to determine whether there were any substantial differences in the rates of the chlorination reactions for the various minerals, which would favour complete chlorination of the niobium and only partial chlorination of the titanium, aluminum and silicon constituents.

APPARATUS FOR CHLORINATION AND PRODUCT SEPARATION

A schematic diagram of the apparatus used in the chlorination study is shown in Figure 1. Several variations of this apparatus design, such as the substitution of a large vertical tube to hold pellets of the charge, were used from time to time, but the principle of the operations was identical and one description will cover all variations.

The principal part of the apparatus was a 1 inch VYCOR reaction tube which was maintained at a constant temperature in a tube furnace. The charge was contained in a silica boat placed in this reaction tube. Over the heated charge, either argon or chlorine was passed at rates determined by flow-meters inserted in the gas delivery lines.

The product of the reaction was a mixture of iron, titanium, niobium, aluminum, calcium, sodium, magnesium, and silicon chlorides. Calcium, sodium and magnesium chlorides, because of their low volatility, remained with any unreacted charge.

As the first step in separating the volatile mixed chlorides, the gas stream was passed through a vertical tube containing coarse granules of hot (300°C) sodium chloride(6). Because of the formation of a low vapour pressure, low melting eutectic of $NaCl-AlCl_3-FeCl_3$, the aluminum chloride and ferric chloride were effectively removed from the gas stream.

In the next stage of processing, the metal chloride gases were passed through a bed of coarse carbon. Additional chlorine was supplied, and any oxychlorides present in the mixed gases were converted to normal chlorides.

Selective condensation was then used to separate the niobium pentachloride from the more volatile titanium tetrachloride, silicon tetrachloride, and excess chlorine, carbon monoxide and carbon dioxide.

In the initial experiments done to study the effects of the variables on the extraction of niobium, the results of the experiments were judged from the analysis of the residue in the silica boat. In subsequent experiments, all products were collected for the determination of metallurgical balances.

RESULTS

Variables Affecting the Extraction of Niobium

In the first group of experiments, the amount of chlorine admitted to the sample was varied, and the effect of this change on the extraction of the various constituents was observed. As a point of reference, the stoichiometric quantity of chlorine required for the reactions was calculated on the assumption that all the metallic elements in the concentrate would be converted to chlorides. No chlorine was allotted for the formation of chlorides from non-metallic elements. It was assumed that the amounts of non-metallic elements were small, and that any potential chlorides which might have been formed would be unstable.

The results of experiments done using fractional amounts of the stoichiometric requirement of chlorine are shown in Table 1.

TABLE 1

Extraction as a Function of the Amount of Chlorine Supplied

Conditions: 8.00 g concentrate, 2.00 g carbon, 90 min, 700°C

Expt No.	Cl_2 flow rate (ml/min)	Cl_2 (x stoich)	Extraction (%)				
			Nb*	Fe	Ti	Al	Si
1	10	0.25	23	89	29	23	13
2	20	0.50	41	96	34	26	12
3	32	0.80	89	95	82	46	37
4	40	1.00	100	100	100	--	65

*Combined niobium and tantalum are reported as niobium.

It is of interest to note in Table 1 that the niobium extraction follows the fractional stoichiometry of the chlorine supplied. It is also of interest to note that complete extraction of the niobium is accompanied by complete extraction of the iron and titanium, and that extraction of the aluminum and silicon is not complete.

In the next group of experiments the extraction of the niobium was studied as a function of the amount of carbon present in the charge. It will be noted that these experiments were done using the stoichiometric requirement of chlorine, but this was supplied more rapidly so that any differences in reaction rates might be more apparent. The results of these experiments are shown in Table 2.

TABLE 2

Extraction as a Function of the Amount of Carbon in the Charge

Conditions:
8.00 g concentrate, 120 ml/min Cl_2 for 30 min (stoichiometric amount),
700°C

Expt No.	Wt carbon (g)	Extraction (%)				
		Nb	Fe	Ti	Al	Si
5	2.00	89	86	85	53	22
6	1.00	87	88	83	51	26
7	0.50	78	74	79	33	10
8	0.25	35	59	36	14	5
9	0.12	21	43	6	20	8
10	0.00	0	26	0	16	3

From the same arithmetical calculation used to determine the stoichiometric chlorine requirement, an estimate was made of the carbon requirement for complete reaction, assuming equilibrium for the system CO-C-CO_2(7). This amount is close to 1.0 gram for an 8.0 gram charge of concentrate. The results in Table 2 indicate that the extraction of niobium is not appreciably increased when more than this amount of carbon is used, but when less is used, the extraction of all constituents is decreased. It is of interest to note that in this group of experiments, as in the previous group, the extractions of iron and titanium follow that of niobium closely, except at very low carbon contents. At a low level of carbon, differences in the reactivity of the minerals become very apparent. In the absence of carbon, about one-quarter of the iron and about one-sixth of the aluminum can be chlorinated.

In the next group of experiments, studies were made of the effect on extraction of changes in the time during which a specified amount of chlorine was admitted to the sample. Two chlorine levels were studied, 80 per cent and 100 per cent of the stoichiometric requirement. These amounts were supplied over short periods at rapid flow rates, or over longer periods at slower flow rates. The results of these experiments are shown in Table 3.

TABLE 3

Extraction as a Function of Time at Two Levels of Chlorine Supply

Conditions: 8.00 g concentrate, 2.00 g carbon, 700°C

Expt No.	Chlorine Supplied rate (ml/min)	Chlorine Supplied time (min)	Cl_2 (x stoich)	Extraction (%) Nb	Fe	Ti	Al	Si
11	96	30	0.80	73	84	67	30	20
12	64	45	0.80	80	97	79	42	23
3	32	90	0.80	89	95	82	46	37
13	120	30	1.00	92	91	87	53	40
14	80	45	1.00	95	94	90	60	46
15	40	90	1.00	98	98	100	65	56

It is of interest to note, in Table 3, a general trend which shows that greater extractions were obtained when the chlorine was admitted slowly, than when the same amount was admitted rapidly. The experiments also confirm earlier results to the effect that greater extractions were obtained when amounts of chlorine at least as great as the stoichiometric requirement were used.

In the next group of experiments, the effect of temperature change on the extraction was studied. Identical experiments were made at three different temperatures. The results are shown in Table 4.

TABLE 4

Extraction as a Function of Temperature

Conditions: 8.00 g concentrate, 2.00 g carbon, 700°C,120 ml/min Cl_2 for 30 min

Expt No.	Temp (°C)	Extraction (%)				
		Nb	Fe	Ti	Al	Si
16	500	87	73	72	21	9
17	600	94	79	93	50	28
13	700	92	91	87	53	40

Even though the conditions selected for the experiments in Table 4 do not represent the closest approach to optimum conditions which might be selected on the basis of the results in Table 3, the results do indicate clearly that the niobium reaction is not very temperature sensitive in the range 500-700°C.

Reagent Consumption in the Production of Niobium Pentachloride

The next group of experiments was done to determine the approximate amount of chlorine required to achieve various levels of niobium extraction from the concentrate. When it is assumed that all of the niobium in the mineral is converted to niobium pentachloride,

$$Nb^{*} + 5/2\ Cl_2 = NbCl_5$$

*Nb as present in the mineral lattice

about 1.9 grams of chlorine will be required for reaction with each gram of niobium. The results of a typical group of experiments are shown in Table 5.

TABLE 5

Chlorine Consumption to Achieve Various Niobium Extractions

Conditions: 8.00 g concentrate, 2.00 g carbon, stoichiometric amount of chlorine, 700°C

Expt No.	Temp (°C)	Chlorine supplied (ml/min)	Chlorine supplied (min)	Cl_2 consumed (g)	Cl_2 consumed (g/g) of concentrate	Extn Nb (%)	Cl_2 consumption per g of Nb
18	500	30	120	3.7	0.46	62	4.3
19	500	60	60	3.5	0.43	64	3.9
20	500	120	30	4.0	0.50	71	4.0
21	700	60	60	6.5	0.81	100	4.6
22	700	80	45	6.4	0.80	98	4.7
23	700	120	30	5.9	0.74	89	4.7

The results shown in Table 5 indicate that for 100 per cent extraction of niobium, about 0.81 gram of chlorine is required for each gram of concentrate. When the chlorine requirements are correlated with lesser niobium extractions, it can be shown that the chlorine consumption varies from about 0.67 to 0.83 gram per gram of concentrate for a variety of conditions. For 100 per cent extraction, the amount of chlorine required is 4.6 grams per gram of niobium in the concentrate, and represents about 2.4 times the theoretical amount of 1.9 grams per gram of niobium.

In the next group of experiments, an attempt was made to decrease the chlorine requirement to extract niobium, by prior treatment of the concentrate with strong sulphuric acid(8). The ore concentrate was baked with an equal weight of concentrated sulphuric acid for 3 hours at 250-500°C. Charges of the sulphated material were prepared for chlorination by mixing 2.00 grams of carbon with 8.00 grams of the sulphated concentrate. The results of this group of experiments are shown in Table 6.

TABLE 6

Chlorine Consumption of Sulphated Concentrate

Conditions: 8.00 g sulphated concentrate, 2.00 g carbon, 700°C

Expt No.	Chlorine supplied		Cl_2 consumed (g)	Cl_2 consumed g/g of sulphated concentrate	Extraction Nb (%)	Cl_2 consumption per g of Nb
	rate (ml/min)	time (min)				
24	150	15	4.0	0.50	92.7	5.3
25	90	25	4.4	0.55	97.4	5.6
26	56	40	4.2	0.53	99.5	5.2

The results in Table 6 show that good extractions of niobium from the sulphated concentrate can be expected, even after a short reaction period. It is of interest to note that about fifteen per cent more chlorine is required to extract the niobium from the sulphated concentrate than from the original concentrate.

Attempts to Produce Niobium Oxychloride Exclusively

In the section of this report in which the apparatus was described, reference was made to a secondary stage of chlorination. In this stage, additional chlorine was supplied and the mixed gases were passed through a hot bed of coarse carbon. This treatment served to convert any niobium oxychloride to niobium pentachloride. Whenever this final stage of chlorination was omitted, and the product recovered directly, a mixture of niobium oxychloride and niobium pentachloride was obtained.

Since the work of Fairbrother (9) suggested that niobium oxychloride was quite stable to oxygen, some experiments were done to recover it as the exclusive niobium product. However, it was found that when these procedures were used, the niobium oxychloride was almost invariably recovered as a fine powder. In this form, it was subject to rapid deterioration in the presence of moisture. The material sublimes before melting.

In contrast, it was observed that niobium pentachloride could be melted (mp 209°C) and cast readily in forms having a small surface area to volume ratio. Because of the ease with which cast billets of niobium pentachloride can be protected from moisture, it was considered to be the most suitable product, and experiments on the recovery of niobium oxychloride were discontinued.

Assessment of the Niobium Pentachloride Product

When niobium pentachloride is to be used for the preparation of pure niobium metal, it is essential that the niobium pentachloride be free of niobium oxychloride. When oxygen in this form is present, it is transferred during the reduction, to the niobium metal (10), thereby reducing its grade.

Wet chemical analyses had shown that the impurity levels of other metal chlorides in the niobium pentachloride were satisfactorily low, but no method of directly assessing the oxygen level in the pentachloride was known. The best method of assessing the level of oxygen impurity seemed to be a direct analysis for oxygen of metal produced by reduction of the pentachloride.

The reduction of the pentachloride was made in two stages in the presence of hydrogen (11). In the first stage, the pentachloride was reduced to trichloride, and in the second stage to metal.

$$NbCl_5 + H_2 \overset{550°C}{\rightleftharpoons} NbCl_3 + 2HCl$$

$$NbCl_3 + 3/2\ H_2 \overset{650-825°C}{\rightleftharpoons} Nb + 3\ HCl$$

The progress of the reaction was followed by titration of the liberated HCl. The niobium produced by this procedure contained an appreciable amount of hydrogen which was removed by heating in vacuum at temperatures ranging from 25° to 1000°C for 2 hours. When this metal was analyzed spectroscopically, the constituents shown in Table 7 were found.

TABLE 7

Metallic Impurities Detected in Niobium

Sample	Element (%)					
No.	Ta	Fe	Mg	Si	Ag	Cr
1	n. d.*	0.02	0.03	0.03	0.002	0.003
2	n. d.	0.02	0.006	0.006	trace	n. d.

*n. d. = not detected

The low level of metallic impurities in the niobium metal confirms the results obtained by wet chemical analysis of the pentachloride, to the effect that a good separation of other metallic chlorides from the niobium pentachloride had been achieved. One sample of the metal was analyzed for hydrogen, nitrogen and oxygen, and it was found to contain 0.001 per cent, 0.015 per cent and 0.018 per cent of each constituent respectively. These are about the same levels as in commercially acceptable niobium.

CONCLUSIONS

1. Concentrate prepared from Columbium Mining Products Limited ore was amenable to chlorination treatment.

2. No appreciable selectivity was obtained in the chlorination. Most of the major chlorine consuming constituents were completely chlorinated.

3. The mixed chlorides could be separated readily and quantitatively by distillation and selective condensation.

4. Niobium oxychloride and niobium pentachloride were probably produced simultaneously by the chlorination treatment. The niobium oxychloride could be eliminated quantitatively from the niobium pentachloride by passing the mixed gases, with excess chlorine, through a bed of hot carbon. The niobium oxychloride was converted to niobium pentachloride.

5. Reagent consumption and conditions for the production of niobium pentachloride were as follows:

   0.81 gram of chlorine per gram of concentrate (4.6 grams per gram of niobium) 1.0 gram of carbon per gram of concentrate, temperatures between 600° and 700°C for 30-120 minutes for concentrate particles of 90 per cent -200 mesh.

6. Presulphation of the concentrate did not decrease the chlorine requirement to produce niobium pentachloride.

7. The niobium pentachloride was judged to be suitable for the preparation of niobium metal.

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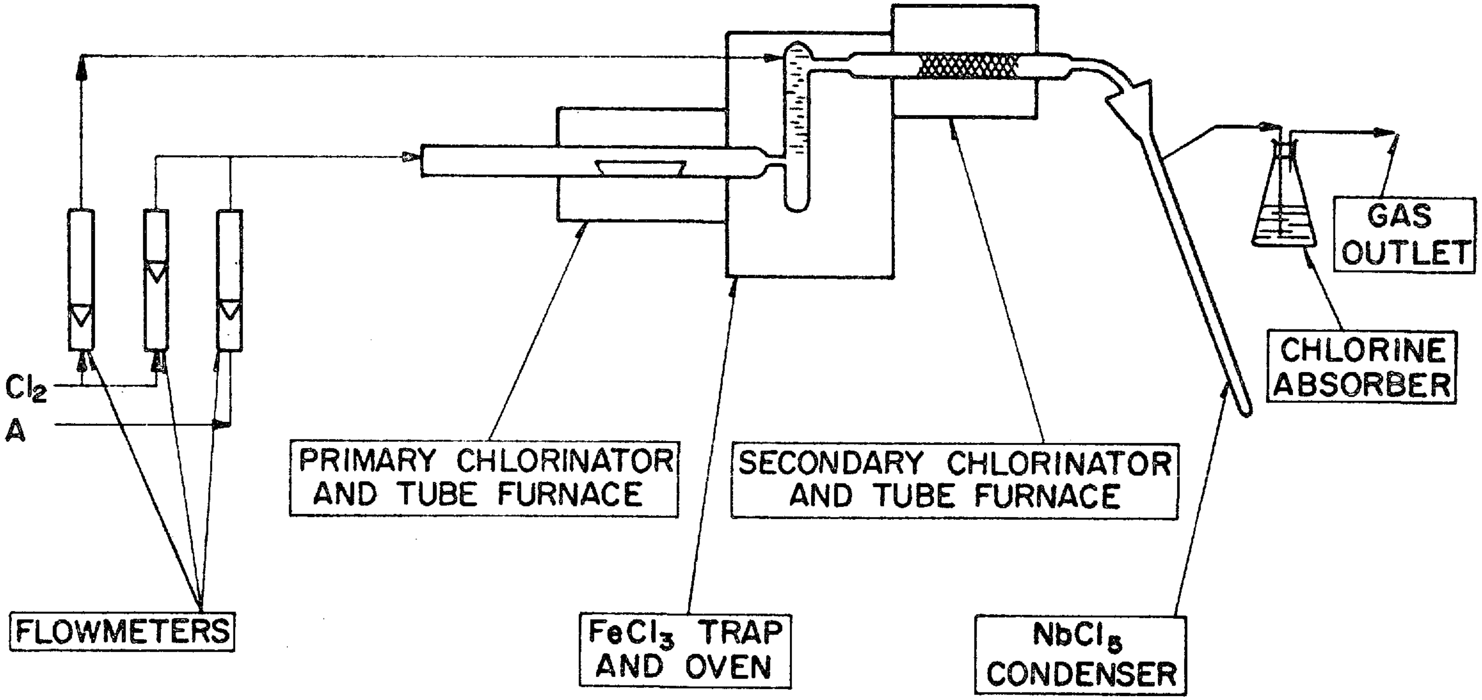

Figure 1 Apparatus used in chlorination experiments