ON THE MECHANISM OF NICKEL SEGREGATION
FROM GARNIERITE ORE

Keizo OKAMOTO* Yasuaki UEDA** Fumio NOGUCHI***

(Received October 19, 1970)

ABSTRACT

The reducing mechanism for recovering nickel from garnierite ore by the segregation-magnetic separation process is described in this paper both from the chemical reaction and physical phenomena points of view.

By segregation roasting, metallic nickel as well as iron and cobalt are reduced both by direct reduction in situ and a combination of chlorination, volatilization and hydrogen reduction of the vapors.

The ratio of the earned metal of the two processes depends on the operating conditions including temperature, retention time and blended reagents such as reductants, water vapor and mixed chlorides.

For optimum segregation, garnierite ore calcined at about 900°C is better than raw ore because faster chlorination can be obtained when compared with low speed of direct reduction at a processing temperature range from 950°C to 1000°C.

Physical phenomena such as formation of fused mixed chlorides, their vaporization, minerallizing effects of vapor and melts, preferential adsorption of chloride vapors on carbon, metals or gangue and formation of metallic whiskers and their growth were studied by *XMA* and electron beam scanning microscope of the segregated particles after separation by means of magnetic concentration method.

1 INTRODUCTION

The segregation process of copper oxide ore is a technique which was accidentally discovered by Moulden & Tapline in 1923 and it was first reported by M. Rey at the VII International Congress of Mining and Metallurgy in 1935[1]. Since then, many workers have investigated this process with shaft furnace, rotary kiln and other equipment. However, the TORCO process which comprises a fluidized bed roaster and a sealed, vertical tube reactor has been developed recently and it has been proved that this is successful in commercial operation

Department of Metallurgy, Kyushu Institute of Technology
* Professor, ** Associate Professor, *** Research Assistant

[2] [3]. The design of this plant and the history of these investigations have been reported by M. Rey[4]. Numerous investigations have been carried out during the past few years in Japan and the authors also have investigted this process for utilization in recovery of nickel in lateritic iron ore and nickel oxide ore from 1962. The experiments have chiefly been carried out on the reaction mechanism from the standpoint of chloridizing metallurgy[5].

Hitherto, the mechanism of segregation has been explained only from the point of view of chemical reaction and there are no literature on migration and precipitation on carbon of nickel and copper in ores, the so-called segregation mehanism.

2 CHEMISTRY OF THE SEGREGATION PROCESS

When copper and nickel oxide ores are heated with a small amount of halide salt and a reducing agent to a suitable temperature, metallic copper and nickel from the ores migrate to the surface of of the reducing agent.

In this chemical reaction, hydrogen chloride gas is produced, chlorination of oxides and their volatilization take place, and these chloride vapors are reduced to metal with H_2 gas. M. Rey's theory of this process which has been widely accepted can be explained by the following reactins.

$$(1) \quad SiO_2 + H_2O + 2NaCl \rightarrow 2HCl + Na_2SiO_3$$

The combined water and silica in the ore are useful for decomposing halides and the hydrochloric acid formed by the reaction chloridizes the metallic oxides in the ore.

$$(2) \quad NiO + 2HCl \rightarrow NiCl_2 + H_2O$$
$$Cu_2O + 2HCl \rightarrow Cu_2Cl_2 + H_2O$$
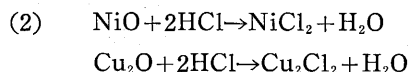
The water vapor formed by the chloridizing step produces H_2, CO and CO_2 gases by reacting with the carbon which has been added. The H_2 gas reduces the copper and nickel chlorides to metal readily.

$$(3) \quad NiCl_2 + H_2 \rightarrow Ni + 2HCl$$
$$Cu_2Cl_2 + H_2 \rightarrow 2Cu + 2HCl$$
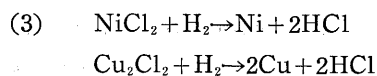
The chemistry of these reactins has previously been reported by Bagdasarian[6] with respect to copper. He has found that the metallic copper is reduced from the chloride in a vapor state at 400°C, at which the vapor pressure is below 1 mmHg. The same mechanism can be considered for nickel chloride because it has sublimation property.

As shown in Table 1, the reaction between chloride and H_2 gas progresses even at a low H_2 partial pressure, especially at higher temperatures.

Table 1. Relation Between Reduction of Chlorides by H_2 Gas and Gas Composition at Equilibrium.

	(3,1)$NiCl_2(g)+H_2\rightarrow Ni(\beta)+2HCl(g)$				(3,2)$Cu_2Cl_2(g)+H_2\rightarrow 2Cu(s)+2HCl(g)$			
Temp. °K	973	1073	1173	1273	973	1073	1173	1273
$\Delta G°$, Kcal	$-5,266$	$-8,718$	$-12,134$	$-14,996$	$-9,014$	$-11,293$	$-13,541$	$-15,731$
P_{HCl}, %	94.2	98.4	99.5	99.8	99.05	99.50	99.70	99.80
P_{H2}, %	5.8	1.6	0.5	0.2	0.95	0.50	0.30	0.20

The HCl gas formed by this reaction can be used again for chlorination of metallic oxide in Eq. (2). In such segregation process, a smaller amount of the chloridizing agent than the stoichiometric amount is required for converting all oxides to chlorides because it is a regeneration-recycle process.

Changing the oxides to chlorides by producing hydrogen chloride by using chloridizing agent is a simple chloridizing roasting process. However, if regeneration and recycle of hydrogen chloride gas to the reaction which takes place among metallic oxide, chloridizing agent and reducing agent are considered, this reaction can be said to be a special chloridizing process.

For instance, if Eqs. (2) and (3) are combined, this reaction is simply reduction of oxides by hydrogen.
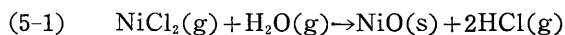
(4-1) $NiO+H_2\rightarrow Ni+H_2O$

(4-2) $Cu_2O+H_2\rightarrow 2Cu+H_2O$
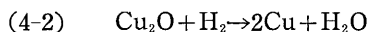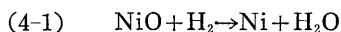
Therefore, direct reduction by H_2 gas is completely inhibited to ensure good segregation, and the reaction progresses by the so-called roundabout reduction of metallic oxide→chloride→vaporization of chloride→H_2 reduction.

These reactions depend on selection of suitable conditions such as temperature range, kinds and amounts of salt, blending method and amounts of reducing agent, and a suitable ratio of H_2/HCl gases.
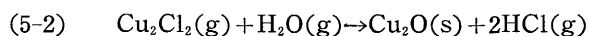
3 ROLE OF ADDITIVES

If excess water is present in the prepared sample, hydrolysis of the chlorides formed by the reaction takes place. On the other hand, if an excess of carbon is present, the amounts of H_2 and CO gases increase by the water gas reaction.

The hydrolysis constants of nickel and copper chlorides are as follows:

(5-1) $NiCl_2(g)+H_2O(g)\rightarrow NiO(s)+2HCl(g)$

$\Delta G°=-4551$ Kcal, Kp=4.96

(5-2) $Cu_2Cl_2(g)+H_2O(g)\rightarrow Cu_2O(s)+2HCl(g)$

$\Delta G°=+6933$ Kcal, Kp=6.45×10^{-2}

It can be seen from the above that there is possibility of hydrolysis of nickel chloride when the water content is high, although there is no problom with copper chloride.

Water present in the segation process is believed to be due to the following:

    (a) Free moisture and combined water in ore

    (b) Water formed by combustion of fuel

    (c) Water formed by chlorination of oxide in Eq. (2).

Now, if water in the ore is removed by calcination, the charge preheated and dehydrated and a sealed reactor is used, water due to (a) and (b) can be eliminated.

Water due to (c) consumes a large amount of salt and the amount of HCl gas becomes large. As a result of this, not only chlorination of NiO and Cu_2O but also of MgO and Fe_2O_3 takes place and water gas reaction takes place between the coexisting reducing agent and water vapor.

The reaction equations and equilibrium constants are as follows:

    (6) $C + 2H_2O \rightarrow CO_2 + 2H_2$ (7) $C + H_2O \rightarrow CO + H_2$ Remarks

|	Kp (6)	Kp (7)	Kp(5-1)
800°C	9.18	7.64	–
900°C	23.6	27.7	–
1000°C	52.3	82.0	4.96

Eq. (6) progresses preferentially at 800°C level and Eq. (7) from 900°C level and both reactions progress more preferentially than hydrolysis of nickel chloride at 1000°C. Therefore, it is difficult for hydrolysis of nickel chloride to take place in the presence of reducing agent.

Although hydrolysis is an important reaction in the segregation process, if an excess reducing agent is present in the system, the water gas reactins of Eq. (6) and Eq. (7) take place easily. This increase in H_2 and CO contents makes localized direct reduction of Eq. (4) take place easily.

However, as shown by the experimental results in next chapter, the chloridizing reaction rate by HCl gas is faster than reduction by H_2 in a temperature range from 900°C to 1000°C. If garnierite is dehydrated by calcining as in the TORCO process, satisfactory segregation can be obtained in a temperature range from 900°C to 1000°C.

3-1 Mixing Amounts of Reducing Agent

The segregation reaction is simply the foliowing reaction:

    $NiO + C \rightarrow Ni + CO$
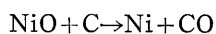
Consequntly, the amount of reducing agent required will be 1/10~1/5 of the nickel content. It is clear from the chemical analysis of the segregated particles

formed on carbon that depending on the temperature, a large amount of iron and almost all cobalt in the raw material are found with nickel. It can therefore be assumed that these metals are also reduced by the same mechanism. Moreover, it is necessary to make the amount of reducing agent a little larger than the stoichiometric quantity because a part of it is required for formation of metal nuclei at the start and subsequent migration of metal on them.

According to a report on the TORCO process, there is an example of use of 2.5 % reducing agent in case of copper content of $2{\sim}3$ % but at a temperature level of 800°C the reduction of copper oxide takes place as follows:

$$2Cu_2O + C \rightarrow 4Cu + CO_2$$
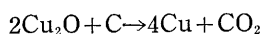
Therefore although the stoichiometric amout of reducing agent is about 1/20 of the copper content, an amount $2{\sim}3$ times this is used.

3-2 Influence of Moisture

Water vapor is effective for decomposition of salt and production of HCl gas. Once HCl gas is produced in a sealed reactor heated externally, the combined reactions of Ep. (2) and Eq. (3) take place as long as oxides are present in the system and additional water vapor is not necessary because this is a repeating, regenerating reaction.

It has been reported that good yield was obtained when segregation was carried out after pelletizing, drying and preheating the charge with indirect heating system but the result was poor when direct heating in which combustion gas contacted the ore directly[7]. The hot combustion gas not only prevents repeated regeneration of HCl gas but as moisture over 10% is produced by heavy oil combustion, it tends to increase the proportion of direct reduction when excess reducing agent is present together.

3.3 Amount of Chloridizing Agent

The most important additive in the segregation process is chloridizing agent. When ore is heated in a sealed, externally heated reactor, the required amount of salt is much less than the stoichiometric amount because of HCl gas formation and HCl gas regeneration cycle.

In case of copper oxide ore, it appears that a slightly larger quantity of salt is required for successful segregation when the ore is basic and lime content is high. Iron oxide and magnesia in garnierite ore are chloridized easily and consequently, a somewhat larger amount of salt is required. However, it must be noted that HCl gas is supplied by decomposition of $FeCl_2$ and $MgCl_2$ at a high temperature.

When segregation experiments are carried out by adding excess salt and with short retention time, undecomposed salt remains in the calcined product. More-

over, there were cases in which the salt did not decompose but vaporized at a higher temperature and condensed on the cold part of the reaction tube. These results were confirmed by x-ray analysis of the calcined and deposited products or from analytical results of Fe^{++} and Mg^{++} in the soluble chlorides. Furthermore, as can be seen from the vapor pressure in Fig. 8, $CaCl_2$ appears to be a more effective chloridizing agent than NaCl for garnierite segregation at a high temperature.

As indicated above, addition of a very small amount of chloridizing agent is sufficient but chloridizing reaction is promoted with a large addition rate and the proportion of direct reduction becomes small. Consequently, the proportion of roundabout reaction becomes large and the segregation results indicate a tendency of growth of precipitated metal, increase in yield and higher nickel content. These points will be explained in Chapter **5** as physical phenomena.

4 COMPARISON BETWEEN CHLORIDIZIND REACTION AND REDUCING REACTION OF VARIOUS GARNIERITE ORES

As mentioned above, in the segregation process NiO is not reduced directly to metal by H_2 gas but it must be first chloridized by liberated HCl gas and the $NiCl_2$ produced is reduced to metal by H_2 gas. Experiments were carried out to clarify these relations by comparing the reactivities of Eq. (2) in which oxide is chloridized with HCl and of Eq. (4) in which the oxide is reduced with H_2.

As samples, raw Weil and Celebes ores were calcined at various temperatures for 2 hr. to dehydrate the ores.

The chemical analysis of these garnierite ores are given in Table 2.

Table 2.   Chemical Composition of Samples (%).

Sample	Fe	Ni	Mn	SiO$_2$	MgO	Al$_2$O$_3$	CaO	Ig. Loss
Celebes Ore	11.28	2.98	0.17	43.00	20.83	0.38	2.24	14.6
Weil Ore	17.76	3.05	0.26	32.16	22.04	0.54	3.08	15.2

A small amount of the sample was weighed in an Al_2O_3 boat and placed in a quartz tube with one end closed. The temperature was increased to the specified value in 30 minutes in an argon atmosphere and the reaction was carried out in a H_2 or HCl gas stream for a fixed time. After the reaction has been completed, argon gas was introduced to remove the H_2 or HCl gas from the reaction tube. The furnace was removed rapidly to cool the tube, the boat taken out, the heated sample in the boat weighed, and then, chlorides and metals were analyzed for Fe, Ni and MgO. Also, volatilization loss was calculated by using these results.

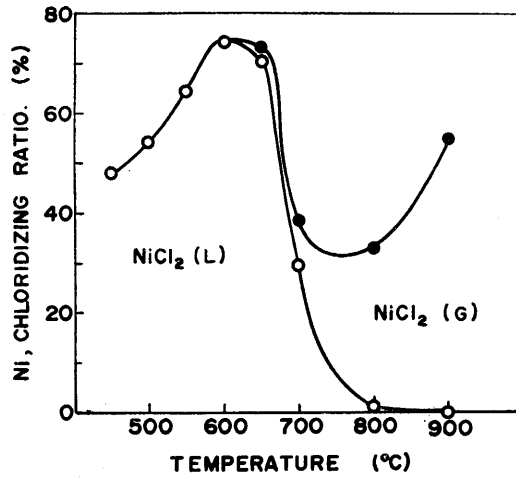In the preliminary experiment, 1.0~1.5 g of the sample was taken for chemical

Fig. 1. Relation between chloridizing ratio of nickel and heating temperature. (Celebes raw ore, Ni=2.98 %) (L). Soluble. (G). Vaporized.
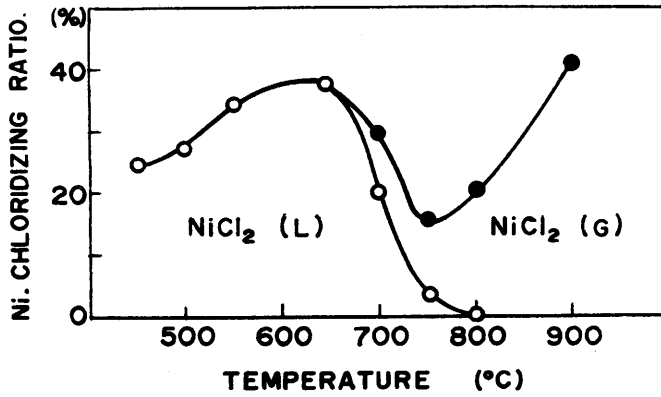

Fig. 2. Relation between chloridizing ratio of nickel and heating temperature. Calcined Celebes ore, 775°C. Ni=3.42%) (L). Soluble. (G). Vaporized.

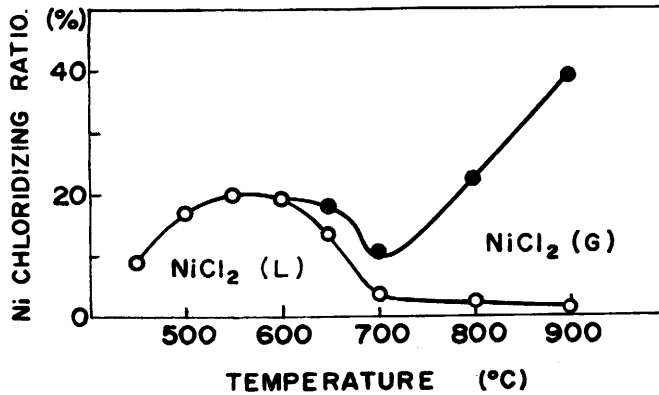
Fig. 3. Relation between chloridizing ratio of nickel and heating temperature; (Calcined Celebes ore, 900°C Ni=3.39%). (L). Soluble. (G). Vaporized.
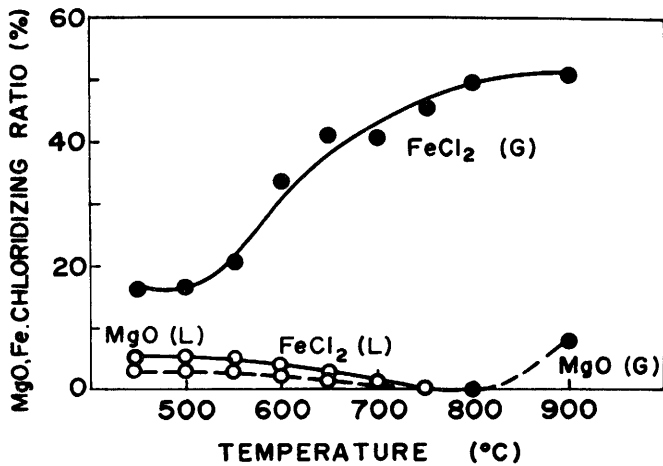
(29)

Fig. 4. Relation between chloridizing ratio of Fe, MgO and heating temperature. (Weil ore, Fe=17.76%, MgO= 22.04%) (L). Soluble. (G). Vaporized.
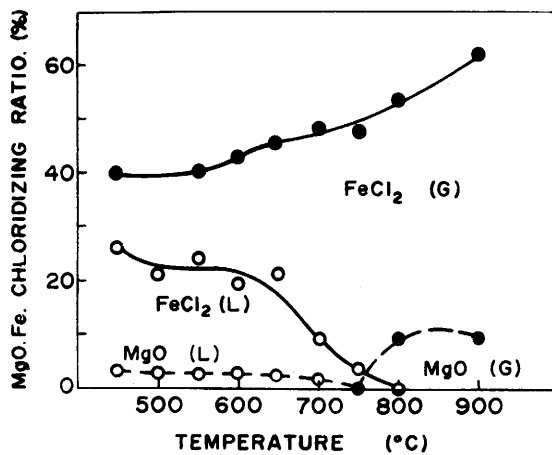

Fig. 5. Relation between chloridizing ratio of Fe, MgO and heating temperature. (Celebes ore, Fe=11.28%, MgO=20.82%) (L). Soluble. (G). Vaporized.

analysis of the segregated ore. The flow rate of HCl was 43 cc/min and the retention time was 30 min. The results are shown in Figs. 1, 2, 3, 4 and 5. In the chlorination of the various calcined ores prepared from two kinds of garnierite ores, 0.5g of the sample was weighed, the flow rate of HCl made 50 cc/min, and the retention time was 30 min. The results are shown in Figs. 6 and 7.

In the reduction by H_2, 0.5 g of the sample was also weighed, the flow rate of H_2 made 100 cc/min, and retention time was 60 min. The results are shown with dotted lines in Figs. 6 and 7.

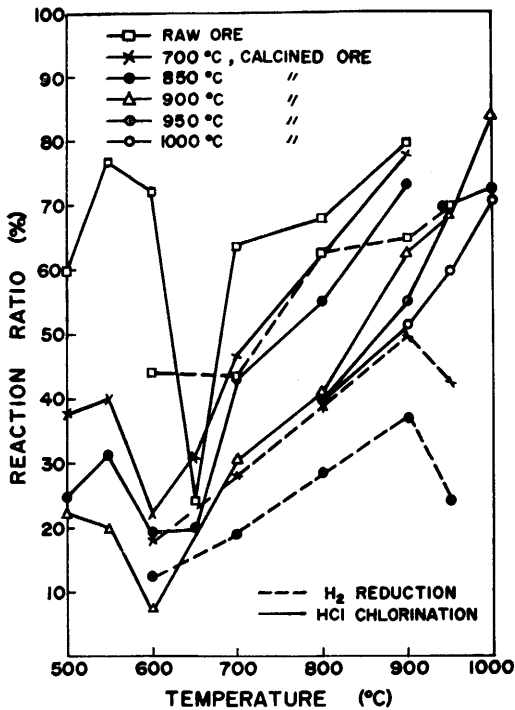The results obtained from these figures are summarized as follows.

Fig. 6. Comparison between H_2 reduction and HCl chlorination ratio at various temperatures. (Celebes ore.)
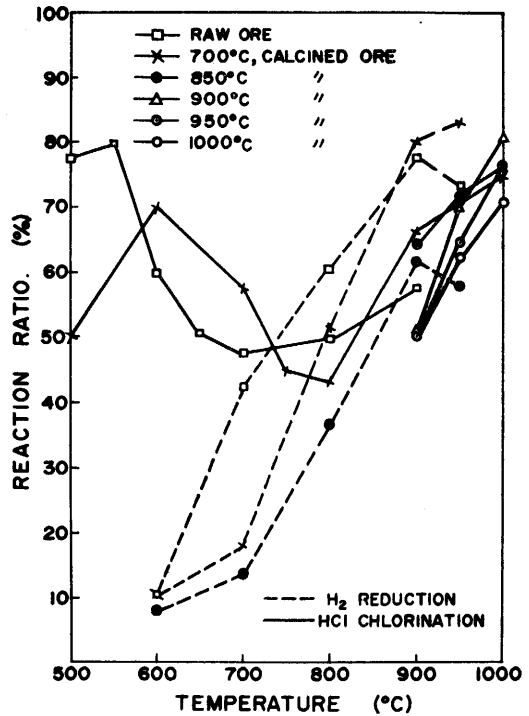
Fig. 7. Comparison between H_2 reduction and HCl chlorination ratio at various temperature. (Weil ore.)

(1) Chloridizing rate of nickel was slightly higher than in the preliminary test but it is believd that this is due to the lower flow rate of HCl gas (43 cc/min to 45 cc/min) and larger amount of sample (sample in the boat becomes 2~3 times thicker). However, the relation between chloridizing rate and temperature indicated the same tendency in all results.

(2) Chloridizing rate increases with increase in temperature but drops in the temperature range from 700°C to 800°C and increases again sharply from above 800°C.

(3) Vaporization of $NiCl_2$ increases at a higher temperature and chloridizing rate increases linearly. In the preliminary experiment, measurements were made up to 900°C but as shown in Figs. 6 and 7, the same experiment was carried out continuously with the various calcined ores at 950°C and 1000°C. The results indicated that HCl chloridizing rate is faster and H_2 reducing rate is slower at above 950°C.

(4) Chloridizing rate is high at a temperature level of 600°C but decreases with increase in temperature. In case of raw ores, this is due to the influence of hydrolysis by combined water. However, the chloridizing rate decreased even in case of calcined ore which does not contain water. The reason for this is

that the reaction rate decreases with increase in temperature from the relation of *ΔG°-Temp.* of the chloridizing reaction. However, the rate is believed to bei ncreased by increase in the tendency of new reaction surface appearing successively with increase in temperature by vaporization of chloride which has formed.

(5) Reaction rate of calcined ore was lower when compared with raw ore and this became particularly marked at a heating temperature of above 800°C due to formation of forsterite.

(6) When all of the calcined and raw ores were chloridized at temperatures above 800°C, the chloridizing rate increased linearly.

(7) As shown in Figs. 4 and 5 of the preliminary expriment, relation between chloridizing rate and temperature exists not only in case of nickel but also in case of iron oxide and magnesia in the ore and it can be considered that this is to be expected as chlorides formed by reaction of basic ore and HCl gas are volatilized easily in the flowing gas stream. Chloridizing and volatilization of iron were very high iron content in ore. Also, considerable chloridizing and volatilization of MgO were observed at above 900°C.

(8) Next, using the same samples, the gas flow rate and retention time were doubled as reduction was excessive and reaction rate low. NiO is reduced readily in the Mond process but nickel oxide in garnierite ore cannot be reduced so easily. One of the reasons for this is that vaporization of the chlorides formed and appearance of new reaction surface as observed in chloridizing do not take place and NiO is fixed in forsterite[8].

(9) The reaction rate differs to some extent in accordance with the kind of ore. In case of Weil ore, the reducing rate was higher than the chloridizing rate at below 900°C (however, both the flow rate of gas and retention time were doubled) but as can be inferred from the chemical analysis of Table 2, Weil ore consists chiefly of lateritic iron ore when compared with Celebes ore.

(10) The difficult reducibility of nickel in garnierite ore is assumed to be due to the formation of forsterite[8] but all samples, both raw and calcined ores, are difficult to reduce at 950°C irrespective of the source of ore.

(11) The fact that chloridizing becomes difficult the higher the temperature differs from (6) and can be considered as being convenient from the point of view of chemistry of segregation which was considered in the foregoing chapter.

(12) A temperature level of 800°C is suitable for segregation of copper oxide ore but a temperature above 900°C is desirable for garnierite ore. The reason for this is that H_2 reducing rate becomes lower at 950°C but chloridizing rate increases with increase in temperature and the difference between these two rates is larger for calcined ore. It was found by a separate experiment that a suitable roasting temperature is from 900°C to 950°C, and a roasting temperature of 1000°C was slightly too high.

(13) As the measurement of chloridizing rate was carried out in a stream of HCl gas, this measuring condition differs from the condition of the segregation process in which the sample is prepared by mixing ore, reducing coke and chloridizing agent, and pelletizing and heating the pellets in a sealed furnace. When $NiCl_2$ is reduced to metal with a small amount of H_2, however, the vapor pressure approaches zero so that the chloride formed is pushed out and approaches zero and chloridizing progresses on the new reaction surface.   Moreover, H_2 re-duction produces 2 times the number of moles of HCl gas in a sealed furnace, as shown in Eq. (3), so that it resembles the condition in which HCl gas flows.

(14) Segregation process is a special chloridizing metallurgy in which various reactions which are referred to below take place in cycle with respect to each other. The various reactions which can be considered are chlorination by HCl gas, precipitation of metal, regeneration of HCl by H_2 reduction of the chloride formed and formation of H_2 by reaction with a reducing agent, and formation of water vapor by chlorination.   In the cycle of these reactions, the mixing proportions of chloridizing agent, moisture and reducing agent must be kept in balance.   Also, a sealed tube furnace whose temperature can be controlled and regeneration and repetition of reactions mentioned at the end of Chapter 2 are necessary.

5 PHYSICS OF THE SEGREGATION PROCESS

Up to the preceding chapter, the segregation process has been considered as a chemical reaction from the point of view of whether it is a direct reduction or
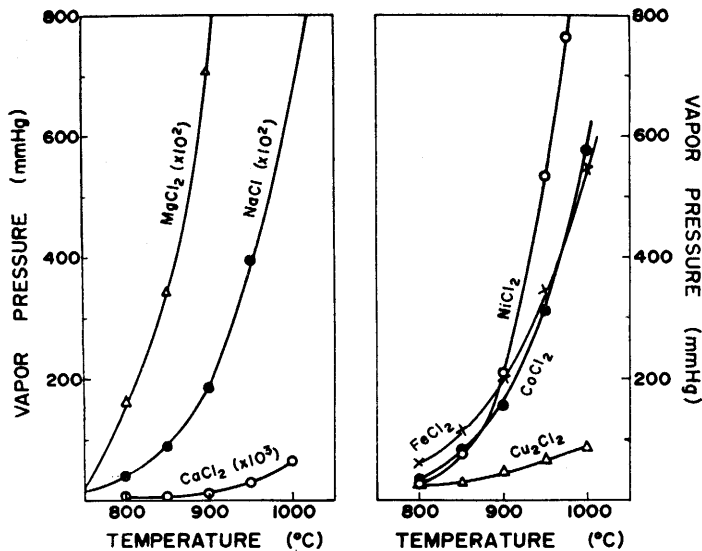

Fig. 8. Vapor pressure of chlorides.

roundabout reduction but the cause of nickel migration, precipitation and growth on the carbon particle have not been discussed as yet.

The vapor pressures of chlorides are shown in Fig. 8 and the melting points of these chlorides are $NiCl_2$ 800°C, $CaCl_2$ 774°C, $MgCl_2$ 714°C, $FeCl_2$ 677°C, $CoCl_2$ 724°C, $CuCl_2$ 430°C, and $NiCl_2$ sublimates easily. These mixtures or formed chlorides easily become mutually mixed, fused salt and some kinds of oxides are melted in it. That is, fused and gaseous zones are formed during the process of increasing the temperature and it has been reported that crystallization of forsterite takes place much easier than expected in the fused zone[9]. This can be considered as the so-called mineralization effect.

Consequently, the correlation of the surface tension of mixed, fused salt melt of the various chlorides, its effect on wettability of chlorides to carbon, metal and gangue, vapor pressure of the various chlorides, the difference in adsorbabilty on carbon and gangue, the effect of metal reduced by H_2 reduction on growth and coarsification on the adsorption sites, and the mode in which iron and cobalt in ore precipitate in the alloy state with nickel are all physical phenomena in the segregation reaction.

Only the chemical reactions have been proposed and especially the reaction velocities of chlorination and reduction have been compared in the preceding chapter. Next, vaporization, adsorption and H_2 reduction of chlorides, growth of precipited metal and alloy composition after the formation of chlorides will be discussed.

5.1 Vaporization and Hydrogen Reduction of Chlorides

Whiskers have been produced by hydrogen reduction of halide salts[10] [11] [12] and Bagdsarian photographed beautiful metallic copper precipitated on the cover of a boat during the measurement of H_2 reduction equilibrium of chlordes[6].

Using these as references, samples were prepared by mixing the chlorides in ratios of $NiCl_2$: $CoCl_2$: $FeCl_2$ = 1 : 1 : 1 and 1 : 0.1 : 4(these correspond approximately to the composition ratio in the treated ore). The sample was placed in a boat (10×10×80 mm) and this was inserted into a quartz or stainless steel reaction tube. After the sample has been heated to dehydrate in an argon stmosphere, the temperature of the furnace was raised rapidly to the specified temperature and a very small amount of H_2 gas was introduced into the reaction tube. Thin plates of copper, iron, nickel and stainless steel 4~5 mm in width, and pieces of carbon electrode and porcelain plate for spectroscopy were placed on the surface of the boat. The vaporized chlorides adhered on the under surface of the thin plates. The coating was thin at a low temperature but thick at a high temperature.

(1) 90 min. at 850°C

Sample with chloride ratio of Fe: Ni: Co=4: 1: 0.1 was heated up to 700°C in an argon atmosphere and then heated rapidly to 850°C in a stream of a very small amount of H_2. The sample was held for 90 min. at this temperature. Silvery metal in fluffy form remained in the bottom of the boat due probably to the fact that a slightly larger amount of hydrogen gas was introduced near the end of introduction.

The condition of the thin plates arranged on the boat was as follows.

Iron: This was coated the best and the coating curled upward to the upper surface of the plate. The thickness of the coating was 1 mm at the middle part.

Copper: The coating was somewhat thin but it was next to iron.

Carbon: The entire surface was coated with thin, silvery coating.

Nickel: The surface was discolored slightly.

Stainless Steel: There was almost no change but a thick whisker of 3 mm in length was deposited at one place on the under surface.

Porcelain: Entirely no trace of precipitation or coating was found.

(2) 90 min. at 930°~950°C, Mixing ratio of chlorides the same as above

The tendency of coating was the same as above. Thickness of coating was in the order of iron, copper and carbon and thickness of coating increased probably due to the higher temperature and longer retention time than (1). There was entirely no coating on pieces of porcelain.

(3) In case of $NiCl_2$ only

At 900~930°C for 60 min., beautiful dendritic crystals precipitated on the copper plate and also, plates of iron, nickel and carbon were coated rather well. However, stainless steel and porcelain plate had very little coating. Also, at 800~810°C for 100 min., thick coating was obtained because of the longer retention time in spite of lower temperature, and the thickness of coating was in the order of iron, copper, carbon and nickel plates. Particularly in case of iron plate, large whiskers have grown on the surface of the boat. At 850°C for 90 min., all plates were coated, although not very thickly. Iron and carbon were coated somewhat better than the other plates. At 910°C for 60 min., thickness of coating was in the order of iron, nickel, carbon, copper and stainless steel, and dendritic crystals of about 2 mm in length were found on iron and nickel plates. At 950°C for 65 min., thickness of coating was in the order of nickel, copper, iron and carbon.

It was made clear from the above experimental results that fluffy, silvery metal remains in the bottom of the boat; there is almost no coating on the pieces of porcelain which was assumed to be the same as gangue material in ore; and it is difficult to coat stainless steel. There is some difference in the condition of coating with flow rate of H_2, temperature and retention time but carbon, iron, copper and nickel can be coated very well.

Different kinds of test pieces were used because even if the metal precipitates on the carbon by reduction of chloride by H_2, the chloride is adsorbed on this metal next and growth of the precipitated metal progresses here by reduction of the chloride by H_2. From these experimental results, it is clear that iron is coated most easily, nickel and copper follow this, and stainless steel is the most difficult to be coated. It has also been reported in the literature that whiskers can be formed easily by using iron boat[13].

5-2 Compsition of Precipitated Nickel Alloy

Change in composition of the aforementioned coating metals by varying the mixing ratio of chlorides, temperature and retention time was investigted with XMA. Fig. 9 to Fig. 13 show typical examples of coatings on nickel plate with a mixture of equivalents of chlorides at various temperatures and with retention time of 60 min. The general tendency of other examples are as follows.

(1) Nickel content is high at a low temperature level of 800°C and iron content increases at a higher temperature of 950°C.

(2) This tendency indicates good agreement with analytical results obtained by XMA on particles which were formed in the segregation process of garnierite ore.

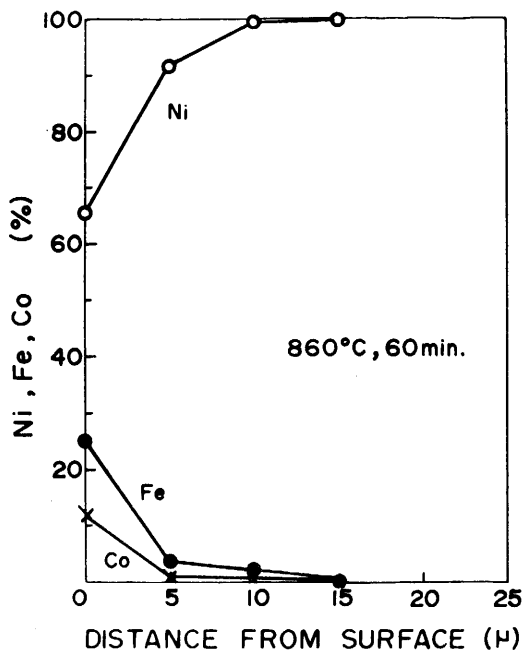(3) Similarly, concentrates obtained by the segregation process-magnetic

Fig. 9. Distribution of nickel, iron and cobalt precipitated on nickel plate.
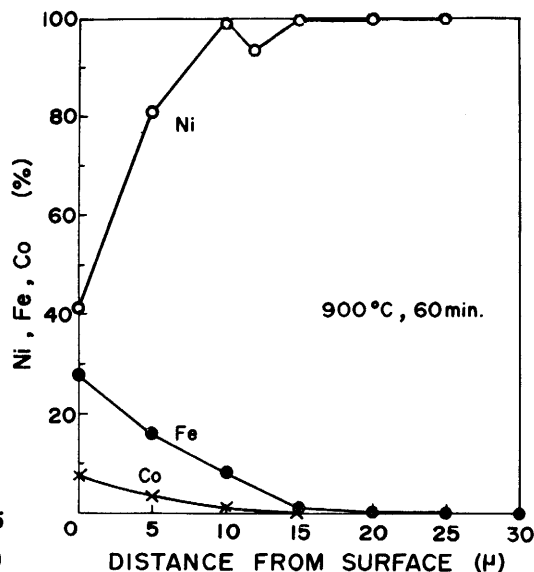
Fig. 10. Distribution of nickel, iron and cobalt precipitated on nickel plate.
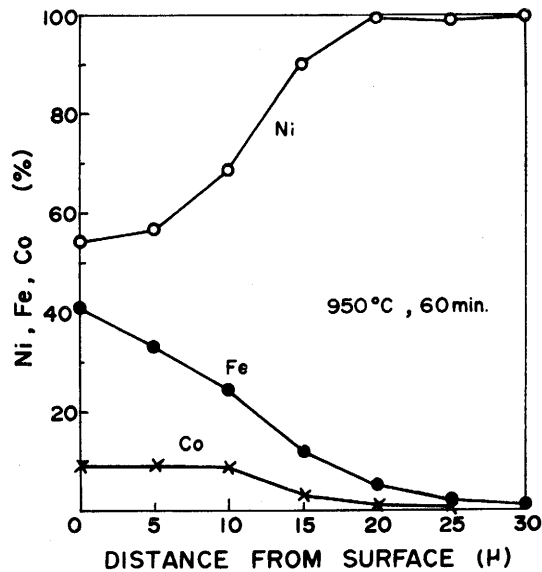
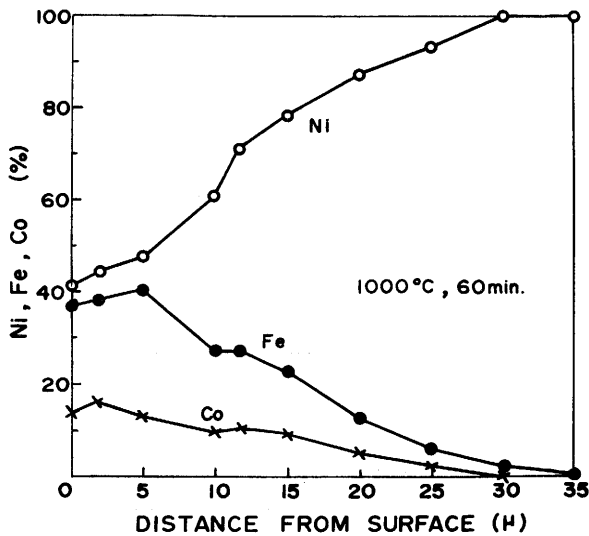Fig. 11. Distribution of nickel, iron and cobalt precipitated
on nickel plate.

Fig. 12. Distribution of nickel, iron and cobalt precipitated
on nickel plate.

separation methed were Fe–Ni alloy from x-ray analysis. The Ni/Fe ratio and
the lattice constant of the alloy differ with the heating temperature and these
results agree very well with the results of chemical analysis.

    (4) Sample with mixing ratio of chlorides of Fe: Ni: Co=4: 1: 0.1 which
was made to resemble raw garnierite ore increased the proportion of iron content
at elevated temperature but the Fe/Ni ratio became half and half at a low tem-

perature of 800°C level.

(5) In this case, Ni/Co ratio became 1/7 at 870°C, 1/6 at 910°C and about 1/3 at 950°C, which differ from the results of mixing ratio of 1/10 of chlorides. However, at a high temperature, the ratios indicated a similar tendency as iron.

The reason for this can be understood to some extent from the vapor pressure curves of Fig. 8.

As indicated in a separate report, a considerably large amount of cobalt was found without any exception by XMA on particles obtained by the segregation process even though the cobalt content in garnierite ore is very small. Therefore, it can be considered that all 3 elements are chloridized, vaporized and reduced by the same mechanism to become alloy particles.

(6) The above-mentioned results were obtained by placing the test pieces on the upper part of the boat but in other experiments, one end of the carbon and metal pieces were inserted into the mixed, fused salt. The pieces were wetted very easily with chlorides and the chlorides curled upward on the pieces by surface tension and the under part of the pieces was coated with a thick alloy layer.
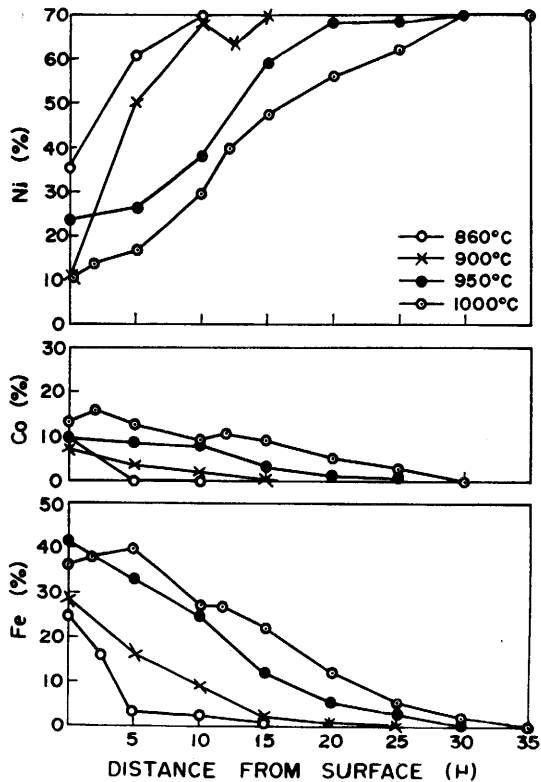

Fig. 13. Relation between heating temperature and distribution of nickel, iron and cobalt.

(7) The decrease in weight of chlorides by decomposition and volatilization was measured previously with a quartz spring balance. When Cu_2O and NiO are mixed with $CaCl_2$ and placed in a Pt basket, the mixed fused salt curls upward from the basket at over 800°C and the edge falls in drops at a higher temperature to make measurement difficult[14].

5-3 Summary of Phenomena Observed from the Physical Viewpoint

Mixed chlorides of nickel, iron and cobalt were volatilized very slowly in a very small amount of H_2 at high temperature and reduction and precipitation on the surface of various metals, carbon and porcelain were carried out. From these results, the order in which adhesion takes place and easiness of coating were investigated; thickness and alloy composition of the cross-section was examined by XMA; and the influences of temperature and others were studied.

In segregation treatment of ore, first HCl gas is produced and chlorination takes place next. The chlorides formed are volatilized and absorbed on coke and are immediately reduced with H_2. Then, adsorption, reduction and growth progress, on the metal surface. Such a process was reproduced in the above-mentioned experiments. With regard to composition analysis by XMA also, it cannot be said that this is applicable to the entire sample as only a certain location and certain particle have been investigated. However, as mentioned at the beginning of this chapter, fused salts of chlorides have good wettability and the vaporized chlorides are easily absorbed. Also, these properties have selectivity with materials as crbon, iron, copper and nickel are easily coated, whereas there is entirely no coating on procelain plate which is similar to gangue. Consequently, the segregation mechanism can be explained very well if both chemical reaction and physical phenomena are considered together. That is, nickel in the oxide ore is chloridized, and nickel is precipitated on the carbon surface by way of mixed, fused salts of chlorides and vaporized gas phase. Then, H_2 reduction takes place on precipitated metal surface, i. e. nickel is not reduced directly from oxide but vaporization, absorption and reduction progress successively. and the particles of reduced metal grow and become coarse. This process of reducing oxide ore is called the segregation process.

As the progress of growth and coarse particle formation of precipitated metal have been investigated in detail with scanning electron microscope, this will be reported in a separate paper.

6 SUMMARY

The segregation process was investigated not only from the point of view of chemical reaction but also from the physical phenomena viewpoint in order to make clear its mechanism. The results obtained are summarized as follows.

(1)　With regard to the chemistry of the segregation process, the mechanism was investigated from the standpoint of chloridizing metallurgy, and this was studied by separating it into direct reduction by H_2 and roundabout reduction in which chloridizing and vaporization take place.

(2)　It was found that the conditions which inhibit direct reduction and give preference to roundabout reduction are moisture, chloridizing agent, reducing agent, heating temperature, etc.

(3)　The reaction rates of chloridizing and reduction were compared with respect to the various raw and calcined ores, and the reason why a temperature range from 900°C to 1000°C is suitable for segregation of nickel in garnierite ore was made clear.

(4)　Our attention was directed to the physical phenomena viewpoint and assumed the following process: fused salts of combined and formed chlorides are produced; vaporization of formed chlorides take place and metal produced by reduction is precipitated on the carbon; and the process of absorption, reduction and growth of particles is repeated.

(5)　As metals other than nickel such as iron, cobalt, etc. in the ore are precipitated by the same mechanism, the precipitated metals are in alloy form and although the composition of the alloy depends on the chemical composition of the raw ore, it is influenced chiefly by the heating temperature.

REFERENCES

(1)　M. Rey; Revue de Metallurgie, Paris. 33 (1936) P 295, 302.
(2)　Pinkney and Plint; Inst. Min. Met. London. 10, June. (1967) C 114, 132.
(3)　Mackey and Gibson; Inst. Min. Met. London. 10, March. (1968) C 19, 31.
(4)　M. Rey; Inst. Min. Met. London. 10, June. (1967) C 101, 107.
(5)　K. Okamoto; J. of Min. Met. Inst. of Japan. Vol. 79 (1963) P 203, 713.
(6)　A. B. Bagdasarian; Ameri. Electrochem. Soc. Vol. 51 (1927) P 449, 494.
(7)　Y. Takahashi et al.; J. of Min. Met. Inst. of Japan. Vol. 83 (1967) P 620, 622, Vol. 84. (1968) P 1372, 1376.
(8)　Y. Shirane; J. of Min. Met. Inst. of Japan. Vol. 84 (1968) P 1368, 1372.
(9)　K. Okamoto et al.; Bull. of the Kyushu Institute of Technology, (Science and Technology) Vol. 21 (1970) P 99, 106, 107, 113.
(10)　P. D. Gorsuch; A. I. M. E. Physical Chemistry of Process Metallurgy. (Part 2) 1959. P 771. (Interscience Pub.)
(11)　D. Sasabe et al.; Procedding of 73 th Iron and Steel Institute of Japan Meeting at Tokyo (1967) 4, P 487, 489.
(12)　J. Nemeth et al.; Cobalt (C. I. C.) No. 45, (1969) P 177, 179.
(13)　Same as (11), (10).
(14)　K. Okamoto; Symposium of Chloridizing Metallurgy, Mining & Metallurgical Institute of Japan (C-Dressing and Extraction Metallurgy) (1963) Oct. P 11, 15.