

The non-oxidative dissolution of nickel mattes in aqueous acidic solutions

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SYNOPSIS

The techniques used in this study of the non-oxidative dissolution rates of high- and low-grade nickel mattes in hydrochloric acid involved leaching and the use of a rotating ring-disc electrode. It was found that the rate of metal dissolution depends on the potential at which the matte dissolves, a maximum rate of dissolution being observed at $-0,2$ V to $0,3$ V (relative to a saturated calomel electrode). The results are comparable with those obtained in work on the dissolution of synthetic nickel and iron sulphides. The adverse effect of excess sulphur on the rate of non-oxidative dissolution is explained in terms of the mixed potential of the reaction. The leaching studies showed the feasibility of processing a high-grade nickel matte by non-oxidative dissolution, and indicate that maximum rates can be obtained in the presence of fairly low concentrations of oxidant. A relative selective dissolution of iron can be obtained from the low-grade matte under reducing conditions, thus resulting in a significant upgrading of this material.

SAMEVATTING

Die tegnieke wat in hierdie studie van nie-oksidatiewe oplostempo's van hoë- en laegrade nikkelmatte in sout-suur gebruik is, behels logging en die gebruik van 'n draairingskyfelektrode. Daar is gevind dat die tempo van metaal-oplossing afhang van die potensiaal waarby die matte oplos en 'n maksimum oplostempo is by $-0,2$ V tot $0,3$ V (relatief tot 'n versadigde kalomelektrode) waargeneem. Die resultate is vergelykbaar met dié wat verkry is in werk i.v.m. die oplossing van sintetiese nikkel- en ystersulfied. Die nadelige uitwerking van oormatige swawel op die tempo van die nie-oksidatiewe oplossing word verklaar in terme van die gemengde potensiaal van die reaksie. Die loogstudies het getoon dat die verwerking van hoëgrade nikkelmatte deur nie-oksidatiewe oplossing uitvoerbaar is en dui daarop dat maksimum tempo's verkry kan word in die teenwoordigheid van redelik lae konsentrasies van die oksideermiddel. 'n Relatief selektiewe oplossing van yster uit die laegrade matte kan onder reduserende toestande verkry word wat 'n beduidende opgradering van hierdie materiaal tot gevolg het.

The Falconbridge matte-leaching process¹ is based upon the selective non-oxidative leaching of nickel from a converter matte containing nickel, copper, and precious metals in metallic and sulphide form. The fraction of the matte smaller than 325 mesh is leached in 7,5 M hydrochloric acid at 70°C for 12 hours, which gives an extraction of 98 per cent of the nickel. Only 2 per cent of the copper present is extracted during this process.

Hydrochloric acid has also been suggested as a leaching reagent for nickel concentrates. Results presented by Van Weert *et al.*² show that 97 per cent of the iron, 70 per cent of the nickel, and 10 per cent of the copper were extracted from a nickeliferous pyrrhotite leached at 70°C in 8M hydrochloric acid for 3 hours. The nickel extracted was in solid solution in the pyrrhotite, whereas the pentlandite remained unleached. Elemental sulphur was found in the residue. Dyson and Scott³ investigated the non-oxidative dissolution of a nickel concentrate in hydrochloric acid. The low nickel extractions recorded (10 per cent) were attributed to the formation of an inhibiting layer of sulphur round the partially leached sulphides. As a possible answer to this problem, the material was activated by being reacted with natural gas at about 750°C. This reduced the sulphur content of the concentrate and, when this material was leached for 1 hour in a boiling solution of 5M hydrochloric acid, 97 per cent of the nickel was extracted.

A fundamental electrochemical study of the dissolution of synthetic nickel sulphides⁴ had indicated that the dissolution rates for pure nickel sulphides depend on the open-circuit potential at which they dissolve. This

potential, which depends on the stoichiometric ratio of the nickel to the sulphur, can be altered to yield a value at which the dissolution rate for nickel reaches its maximum value. Work was therefore undertaken to show whether nickel matte would behave in the same way, and whether conditions could be optimized for the non-oxidative dissolution of such a material. This paper summarizes the results obtained with typical nickel mattes.

Experimental Procedures

Two types of matte were studied: a high-grade matte with the composition $Ni_{1,6}Cu_{0,9}S$, which is a converter matte that was obtained from a local smelter, and a low-grade matte with the composition $Ni_{0,4}Cu_{0,3}Fe_{1,0}S$. Analyses of these materials are given in Table I.

The principal phases present with the high-grade matte were heazlewoodite, chalcocite, and nickel metal, while the low-grade matte contained a nickel-bearing pyrrhotite and an iron-nickel alloy.

The electrochemical measurements were carried out with an assembly⁴ including a rotating ring-disc electrode

TABLE I
ANALYSES OF NICKEL MATTES

Element	Amount, %		Element	Amount, p.p.m.	
	High grade	Low grade		High grade	Low grade
Ni	49,4	15,9	Pt	300	nd
Cu	29,6	14,0	Pd	167	nd
Co	0,26	1,34	Au	48	nd
Fe	0,22	41,9	Rh	17	nd
S	17,3	23,9			

nd = not determined

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in which the disc consisted of nickel matte. An electrode of crushed high-grade matte was prepared with Teflon powder (10 per cent by mass) as the binding agent. The mixture was pressed to form a solid disc that was cut to size and used in the construction of the ring-disc electrode. The collector efficiencies of the silver-ring electrodes were calculated from the dimensions of the electrode⁵.

Sealed glass apparatus was used for the leaching experiments. The leaching vessel contained a two-bladed glass stirrer, a platinum plate electrode, a saturated calomel electrode, a thermometer, and gas inlet and outlet tubes. The vessel was immersed in a water-bath, and temperatures were controlled to within 1°C. During the reaction, a slow flow of high-purity nitrogen was maintained so that the oxygen would be eliminated. In the experiments, hydrochloric acid was introduced into the reaction vessel and, after being deoxygenated, was brought to temperature. The matte was then introduced and stirring commenced. Potentials were monitored with a digital multimeter, and are quoted in this paper relative to the saturated calomel electrode.

The surface areas of the powders were determined according to a standard B.E.T. technique.

The solutions were analysed for nickel, copper, and iron by atomic-absorption spectrophotometry. The metals in the residue were determined by atomic-absorption analysis after they had been digested in acid, and the total sulphur was determined by a Leco combustion technique. In the electrochemical experiments, the hydrogen sulphide was determined by measurement of the oxidation current at the silver ring as it was held at -0,12V.

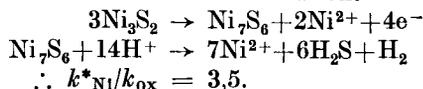
Results and Discussion

Dissolution of High-grade Matte Electrode

The dissolution rates of nickel from the electrode made

from high-grade matte and rotated in 3M hydrochloric acid were found to be linear after an initially fast reaction. The production of hydrogen sulphide, which was monitored continuously as a ring current, decreased gradually with time towards a steady-state value. This behaviour, as illustrated in Fig. 1, is consistent with that reported previously⁴ for synthetic nickel sulphides.

The effect of the reaction variables (potential, temperature, acid concentration, and stirring speed) on the rate of nickel dissolution were investigated with the electrode made from high-grade matte. As can be seen from Table II, the total rate of nickel dissolution (k_{Ni}) increased at increasingly anodic potentials. This rate is made up of two components, however, and, when the component due to direct electrochemical oxidation of the matter (k_{ox}) is subtracted from the overall rate, a value for the rate of non-oxidative dissolution (k^*_{Ni}) is obtained. (The rate of oxidation, k_{ox} , is obtained from the measured current, a two-electron process being assumed.) The rate of non-oxidative dissolution of matte is at its maximum at a potential of approximately -0,2V, and decreases with either anodic or cathodic shifts in potential. This behaviour is reasonably consistent with that reported for synthetic nickel sulphides⁴ and iron sulphides⁶, and can be explained in terms of the formation of a surface with such stoichiometry that the transfer of ions across the solid-solution interface is at its maximum. The potential at which maximum non-oxidative dissolution occurs is slightly anodic to the open-current potential. The ratio of the anodic current to the non-oxidative dissolution rate of nickel was 3,2. This is comparable with the value of 3,5 for the oxidation of heazlewoodite (Ni_3S_2) to Ni_7S_8 prior to non-oxidative dissolution:



Ni_7S_8 was found to dissolve non-oxidatively at a greater

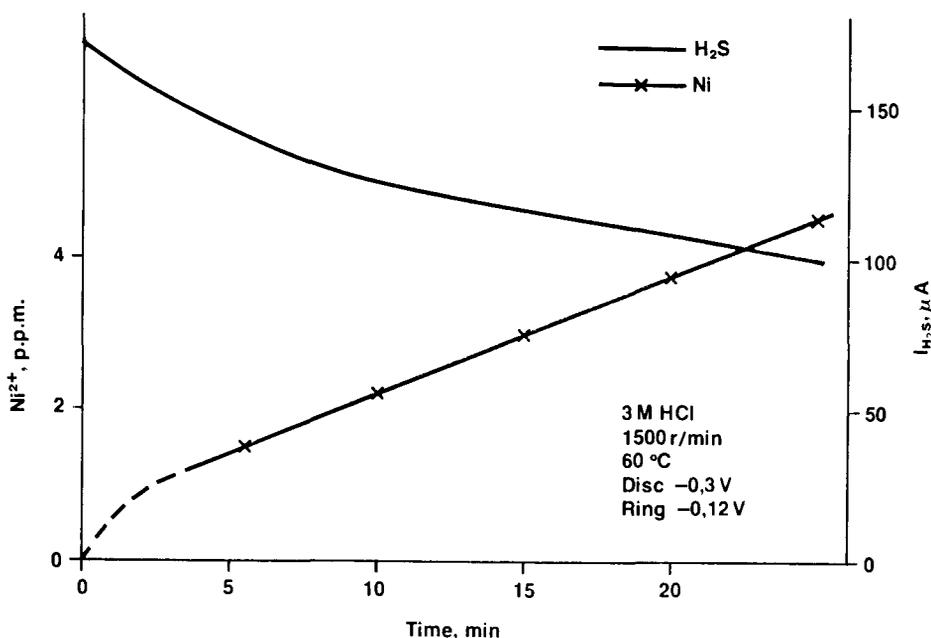


Fig. 1—Rate of dissolution of Ni^{2+} and hydrogen sulphide from high-grade matte (I_{H_2S} is the current recorded at the silver-ring electrode)

TABLE II

EFFECT OF POTENTIAL ON THE DISSOLUTION OF NICKEL MATTE
Conditions: 3M hydrochloric acid, 60°C, 1500 r/min

Potential V(SCE)	$k_{Ni} \times 10^{10}$ mol.cm ⁻² .s ⁻¹	$k_{ox} \times 10^{10}$ mol.cm ⁻² .s ⁻¹	$k^*_{Ni} \times 10^{10}$ mol.cm ⁻² .s ⁻¹	$k_{H_2S} \times 10^{10}$ mol.cm ⁻² .s ⁻¹
-0,1	630	450	180	30
-0,2	420	100	320	70
-0,3	120	42	78	56
-0,4	28	-36	28	90
Open-circuit potential (-0,32)	42	0	42	30
Open-circuit potential (-0,2)†	300	0	—	—

†Adjusted with iron(III) chloride.

rate than nickel sulphides⁴ of any other stoichiometry, and it is therefore reasonable to expect that this also occurs in the dissolution of high-grade matte.

A greater decrease in the rate of non-oxidative dissolution with shift in potential cathodic to the open-circuit potential was recorded for nickel matte than at this potential for synthetic sulphides⁴. This was probably due to the strong potential dependence on the rate of oxidation of nickel metal present in the matte. Thus, at the more cathodic potentials, a nickel-rich phase that underwent slow non-oxidative dissolution was present at the surface. The rate of hydrogen sulphide production (k_{H_2S}) relative to the non-oxidative dissolution of nickel increased with a cathodic shift in potential. It should be noted at this stage that any non-oxidative leaching process should be designed to occur at around -0,2V if the rate of non-oxidative nickel dissolution is to be at a maximum.

When the matte electrode was reacted at its open-circuit potential (-0,32V) in 3M hydrochloric acid, a dissolution rate of $4,2 \times 10^{-9}$ mol.cm⁻².s⁻¹ was recorded.

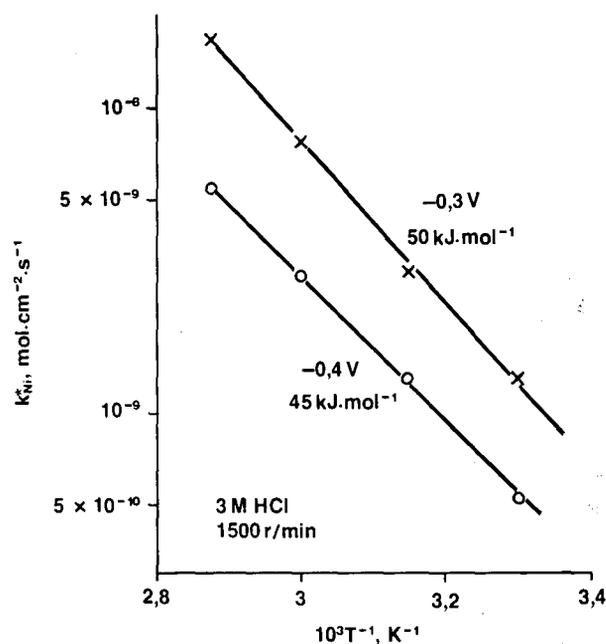


Fig. 2—Activation-energy plots for high-grade matte

The open-circuit potential was then altered to about -0,2V by the addition of iron(III) chloride to the system, and a total dissolution rate of $3,0 \times 10^{-8}$ mol.cm⁻².s⁻¹ was achieved. No attempt was made to discriminate between oxidative and non-oxidative dissolution rates. Thus, a significant enhancement of the dissolution rate was obtained by the addition of an oxidant during the acid-dissolution process. In a process designed to treat a nickel matte of composition similar to that used in this study, the potential of the reaction should be monitored and adjusted to the optimum value for non-oxidative dissolution. This could be achieved by the addition of air or elemental sulphur (see Table VII).

The temperature dependence of the rate of nickel dissolution when the matte electrode is reacted in 3M hydrochloric acid is shown in the form of an Arrhenius plot in Fig. 2. The calculated activation energies are 50 kJ.mol⁻¹ at -0,3V and 45 kJ.mol⁻¹ at -0,4V. These values suggest a predominantly chemical or electrochemical control of the rate of reaction, but are significantly lower than the activation energies recorded⁴ for pure nickel sulphides.

The effect of the hydrochloric acid concentration on the rate of non-oxidative dissolution of nickel at -0,3V follows a power-law dependence, $k^*_{Ni} = [HCl]^{0,85}$, within the concentration range 0,5 to 5M hydrochloric acid (Fig. 3). This increase in reaction rate can be attributed to the increased concentrations of acid and chloride ions. The rate of nickel dissolution also depends on the type of acid used, and decreases in the order HCl > HClO₄ > H₂SO₄ for equivalent acid normalities (Table III). Hydrochloric acid was thought to be the fastest medium because chloride ions facilitated charge transfer across the solid-solution interface. Because of its low pH value, and therefore greater dissociation in aqueous solutions, perchloric acid was faster than sulphuric acid. A similar acid dependence was found for the non-oxidative dissolution of synthetic nickel sulphides⁴.

The rotation speed of the rotating ring-disc electrode made from nickel matte had no significant effect on the dissolution rate of nickel or hydrogen sulphide. The diffusion of products or reactants between the bulk of the solution and the electrode surface is therefore not rate determining an observation that is in agreement with the conclusions drawn from the high activation energy.

An electrode of powdered nickel matte was constructed from Teflon powder and nickel matte smaller than $53\mu\text{m}$ so that the effect of grinding on the non-oxidative dissolution rate of the matte could be noted. Linear nickel-dissolution reactions were observed, there being no significant difference between the non-oxidative dissolution rate of the bulk of the material and that of the powdered matte under open-circuit conditions at $-0,3\text{V}$. Thus, grinding has no effect on the non-oxidative dissolution of nickel-matte electrodes.

Dissolution of Low-grade Matte Electrode

As with the high-grade matte, the dissolution rate of nickel and iron from the low-grade matte was linear with time after an initially fast reaction. However, the total rate of dissolution was considerably greater than that for the high-grade material. Under open-circuit conditions or at cathodic potentials, the rate of iron dissolution was considerably greater than that of nickel.

The maximum non-oxidative dissolution rates were recorded at a potential of $-0,3\text{V}$, which was slightly anodic of the open-circuit potential (Fig. 4). This corresponds to the oxidation of the excess metal in the metal sulphide to form compounds with a stoichiometry that is ideal for non-oxidative dissolution. For synthetic nickel sulphides, this compound was shown⁴ to be Ni_7S_8 , while stoichiometric ferrous sulphide was the

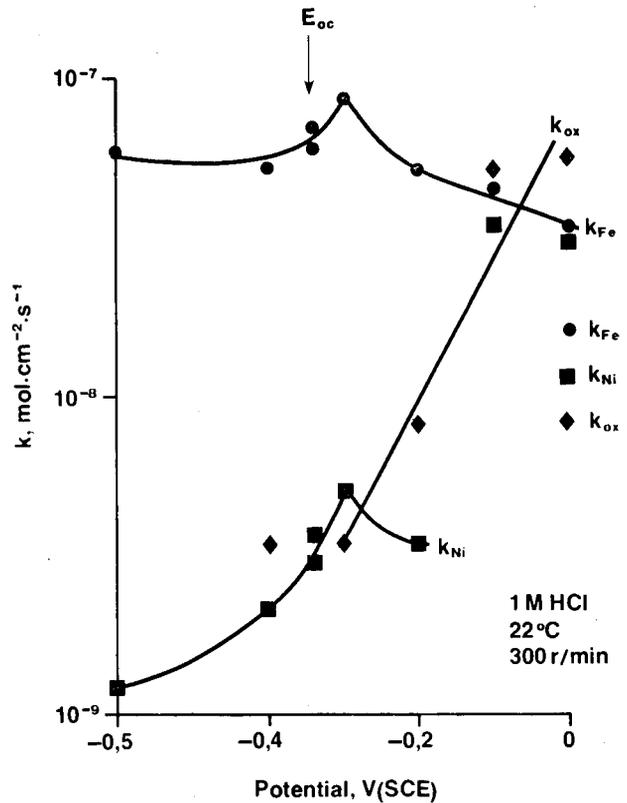


Fig. 4—Potential dependence of the dissolution rates of nickel and iron from low-grade matte

TABLE III

EFFECT OF ACID ON THE DISSOLUTION OF NICKEL MATTE
Conditions: 60°C , 1500 r/min, $-0,3\text{V}$

Acid	$k_{\text{Ni}}^* \times 10^{10}$ $\text{mol.cm}^{-2}.\text{s}^{-1}$	$k_{\text{H}_2\text{S}} \times 10^{10}$ $\text{mol.cm}^{-2}.\text{s}^{-1}$	Measured pH value
3M HCl	120	56	-0,18
3M HClO_4	11	10	-0,20
1,5M H_2SO_4	11	18	0,00
1M HCl	29	5	0,10
1M HClO_4	7	1	0,12
0,5M H_2SO_4	4,2	1	0,67

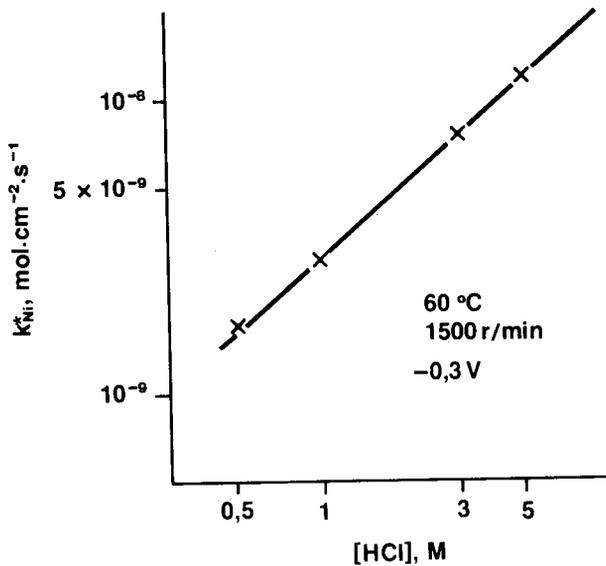


Fig. 3—Dependence of the dissolution rate of nickel from high-grade matte on the acid concentration

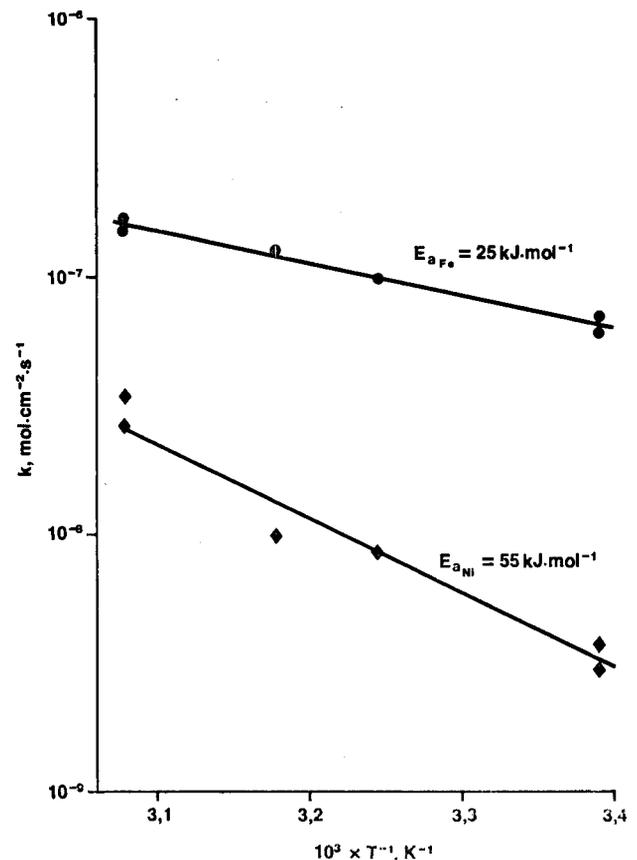


Fig. 5—Activation-energy plots for low-grade matte

most reactive of the iron sulphides⁶. When the potential was shifted anodic to $-0,3V$, the anodic current increased, as did the total rate of nickel dissolution. The total rate of iron dissolution decreased slightly. At potentials of $-0,1V$, the dissolution rates of iron and nickel were comparable under oxidizing conditions. When the non-oxidative component of the dissolution rate at different potentials was approximated, it was apparent that the non-oxidative dissolution rate of both iron and nickel decreased with an anodic shift in potential from $-0,3V$. This can be explained in terms of a decrease in the metal-to-sulphur stoichiometric ratio at the reaction interface under oxidizing conditions, resulting in a slow transfer of ions across the electrical double-layer.

Of principal practical interest in Fig. 4 is the high dissolution rate of iron compared with that of nickel. This means that, under open-circuit conditions, the dissolution of iron from the matte is almost selective. Thus, a low-grade matte could be upgraded by non-oxidative dissolution prior to treatment in the normal manner. Leaching experiments that demonstrate this are discussed later.

The temperature dependence of the dissolution of iron and nickel from the low-grade matte is illustrated in Fig. 5, in which nickel shows an apparent activation energy of 55 kJ.mol^{-1} compared with the value of 25 kJ.mol^{-1} recorded for iron. This shows that the selectivity for non-oxidative dissolution of iron over nickel is minimized at higher temperatures.

The dependence of both the nickel and the iron dissolution rates on the concentration of hydrochloric acid is illustrated in Fig. 6. It follows the expression

$$k_{Fe}, k_{Ni} \propto [HCl]^{0,7}$$

This is similar to the values reported previously for the non-oxidative dissolution of pure nickel sulphides⁴ and iron sulphides⁶.

The dissolution rate of nickel and iron from the matte electrode was independent of the rate of stirring. This implies that the rate of reaction is not controlled by the diffusion of reactants to the reaction site or of products from it. This confirms the previous supposition that the rate of reaction is determined by ion transfer across the Helmholtz double-layer.

Dissolution of Powdered High-grade Matte

When 10 g of the powdered high-grade matte was leached in 350 ml of 3M hydrochloric acid at $60^\circ C$ for 6 hours, 40 per cent of the nickel was extracted (Fig. 7). The rate of nickel dissolution appeared to follow the parabolic reaction kinetics (Fig. 8) that are usually associated with the formation of an inhibiting layer of material round the unreacted core⁷. However, microscopic examination of partially reacted matte did not reveal the presence of any such product layer. The experimental data do not fit the kinetic model for a shrinking core that would be expected in terms of the linear dissolution reaction observed in the electrochemical study. As all the leaching results fitted parabolic rather than linear reaction kinetics, the rate constants

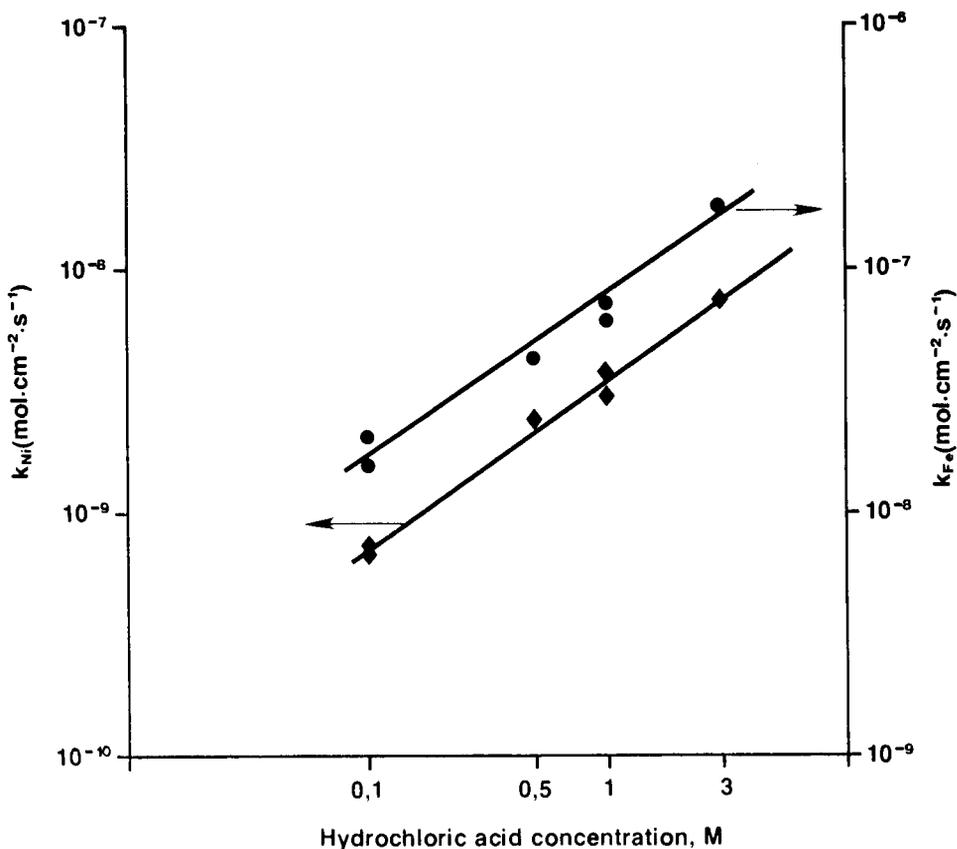


Fig. 6—Dependence of the dissolution rate of low-grade matte on the acid concentration

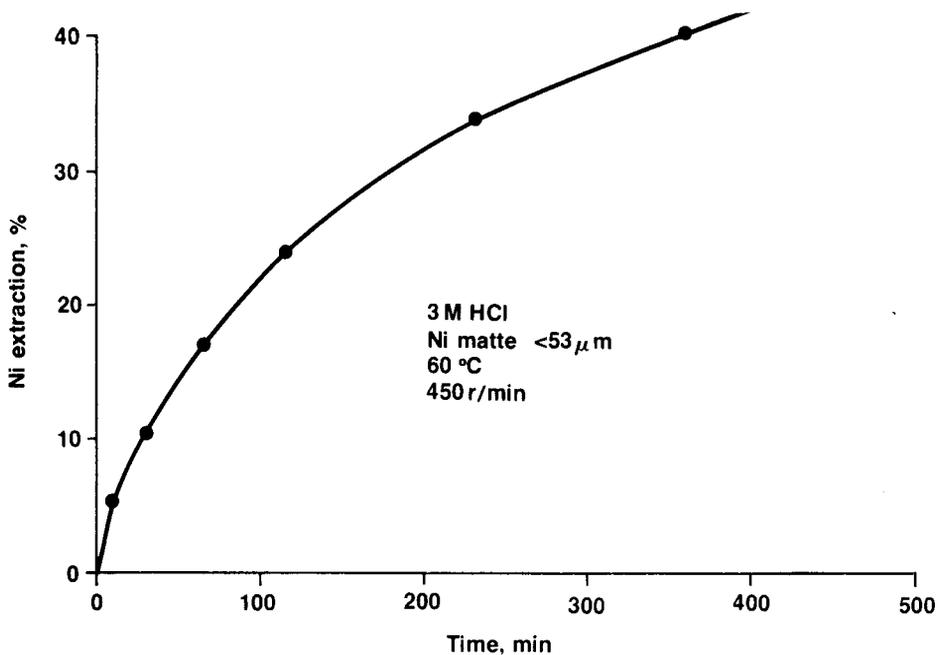


Fig. 7—Nickel extraction from powdered high-grade matte

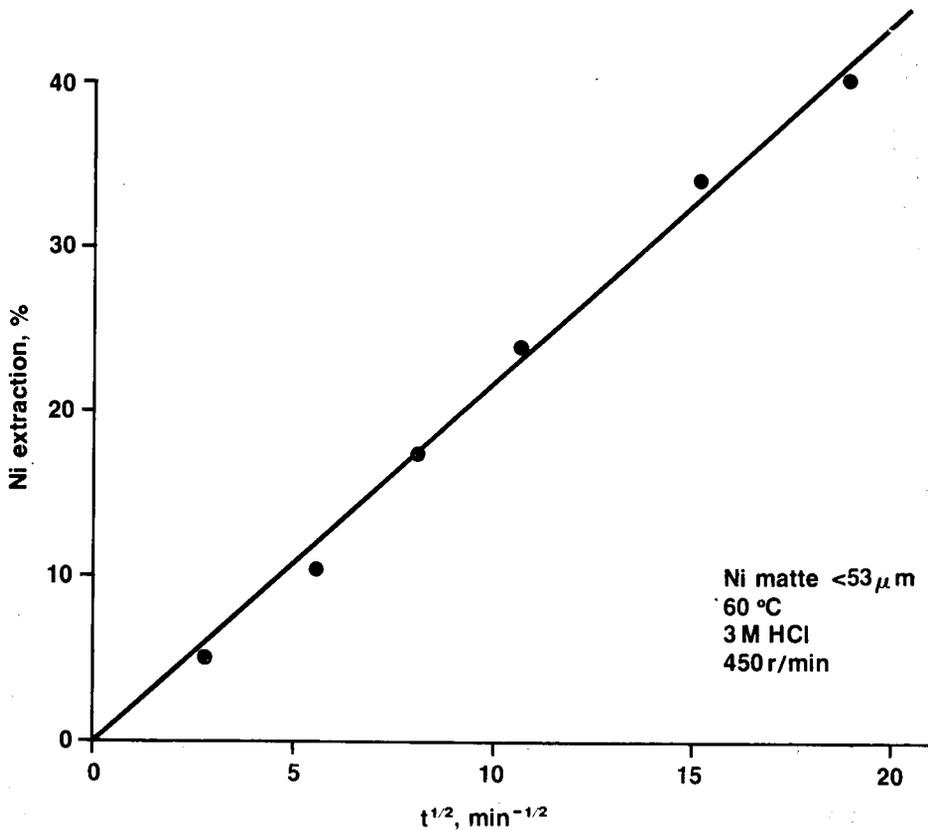


Fig. 8—Nickel extraction versus time for high-grade matte

are quoted in units of $\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}$. No explanation can be offered for the different reaction kinetics observed during the electrochemical and leaching studies.

The dissolution of iron from the matte was initially very fast (35 per cent extraction in 5 minutes), but afterwards did not increase regularly with time. This can be attributed to the fast dissolution of the iron present as pyrrhotite, and the slower subsequent dissolution of the other iron-containing phases. At the beginning of the leach, 2 per cent of the copper dissolved, and this amount remained approximately constant for the duration of the reaction. The presence of hydrogen sulphide ensured that the copper dissolution was minimal.

The effect of acid concentration and type on the rate of metal dissolution during the leaching of nickel matte smaller than $53\ \mu\text{m}$ in size is illustrated in Table IV. The relation between the concentration of hydrochloric acid and the non-oxidative dissolution rate of nickel is not a simple power-law dependence as was observed for the potentiostatted electrodes. This can be explained by the anodic shift in mixed potential towards $-0,2\text{V}$ that was observed at higher concentrations of acid. This anodic shift is attributed to a change, in the metal-to-sulphur stoichiometric ratio at the reaction surface, to a species richer in sulphur. The increased rate of nickel dissolution is due, therefore, to high acid concentration and to the shift in mixed potential. The concentration of chloride ions, which was altered by the addition of sodium chloride, had a significant effect on the rate of nickel dissolution, thus indicating that chloride ion is involved

in the rate-determining step. The dissolution rate showed the same dependence on the type of acid as was found in the electrochemical study, viz $\text{HCl} > \text{HClO}_4 > \text{H}_2\text{SO}_4$.

An activation energy of $40\ \text{kJ}\cdot\text{mol}^{-1}$ was calculated from the leaching results presented in Fig. 9. This is in reasonable agreement with the value of 45 to $50\ \text{kJ}\cdot\text{mol}^{-1}$ that was obtained from the electrochemical study, and again indicates chemical control of the rate-determining step.

The absolute rate of nickel extraction increased slightly with a decrease in the particle size of the nickel matte (Table V). However, the extent of the increase was not directly proportional to the increase in surface area, as is illustrated by the rate constants expressed in terms of $\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$. The apparently higher rate per unit surface area recorded for the fractions of larger

TABLE IV
EFFECT OF ACID ON THE LEACHING OF NICKEL MATTE
Conditions: 60°C , stirring 450 r/min, 3% solids, $<53\ \mu\text{m}$.

Acid	$k_{\text{Ni}} \times 10^8$ $\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$	Potential mV (SCE)
10M HCl	42,6	-230
5M HCl	13,8	-320
3M HCl	7,8	-330
1M HCl	3,9	-360
1M HCl+2M NaCl	5,1	-360
1M HCl+4M NaCl	6,3	-340
3M HClO ₄	4,2	-300
1,5M H ₂ SO ₄	2,1	-360

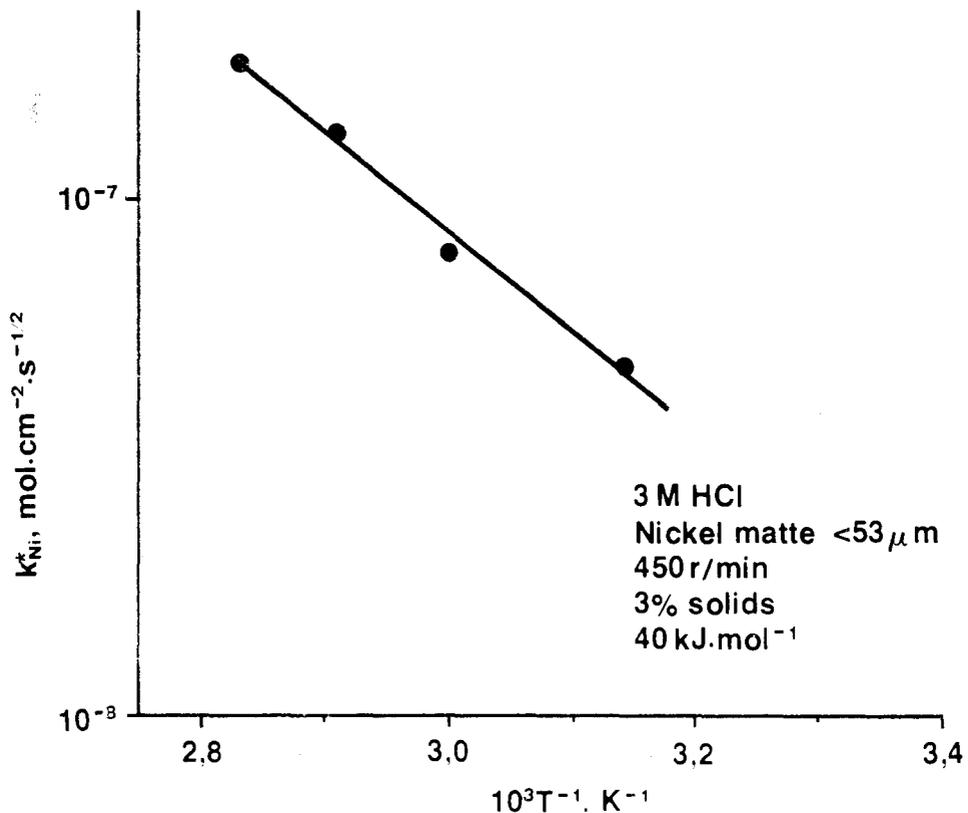


Fig. 9—Activation energy for the leaching of high-grade matte

particle size may be due to the breakdown of these particles during the reaction, resulting in an apparently high reaction rate, or to the different chemical composition and, hence reactivity, of the different size fractions. The difference in reaction rates was not due to different potentials exhibited by the different size fractions of matte. In the processing of the matte by non-oxidative leaching, a slight advantage is gained if the matte is ground to a very fine powder prior to leaching, but this is outweighed by the costs of the grinding.

Stirring speed and pulp density did not have an appreciable effect on the rate of nickel dissolution (Table VI). The reaction rate is not controlled by mass transfer of the reactants or products. When the process is scaled up, the stirring rate should therefore be adjusted to the minimum rate required to maintain the solids in the form of a slurry. The pulp density can be adjusted to yield a pregnant solution suitable for further processing.

The effect of additives to the leach was also investi-

TABLE V

EFFECT OF PARTICLE SIZE ON THE LEACHING OF NICKEL MATTE
Conditions: 3M hydrochloric acid, 60°C, 450 r/min, 3% nickel matte

Particle size μm	k_{Ni} (abs) $\text{mol.s}^{-\frac{1}{2}}$	Surface areas $\text{cm}^2.\text{g}^{-1}$	$k_{\text{Ni}} \times 10^8$ $\text{mol.cm}^{-2}.\text{s}^{-\frac{1}{2}}$
< 53	0,023	2460	7,8
53 to 63	0,022	1460	12,9
63 to 75	0,021	1100	17,1
100 to 200	0,018	—	—

TABLE VI

EFFECT OF STIRRING SPEED AND PULP DENSITY ON RATES OF NICKEL DISSOLUTION

Conditions: 3M hydrochloric acid, 60°C, nickel matte <53 μm

Stirring speed r/min	Solids %	$k_{\text{Ni}} \times 10^8$ $\text{mol.cm}^{-2}.\text{s}^{-\frac{1}{2}}$
450	3,0	7,8
1000	3,0	9,9
1400	3,0	9,9
450	1,5	7,7
450	6,0	7,9

gated. Elemental sulphur, iron powder, and hydrogen sulphide were added separately to the reacting slurry so that their effect on the leaching rate and potential could be observed. The bubbling of hydrogen sulphide through the slurry had no significant effect on the rate of nickel dissolution (Table VII). This is not entirely unexpected, since, as shown by calculation, a concentration of Ni^{2+} higher than 10³M can theoretically co-exist with 0,02M hydrogen sulphide in 3M hydrochloric acid before alpha nickel sulphide is precipitated. Thus, there is no necessity for hydrogen sulphide to be eliminated from the solution for high-equilibrium extraction of nickel to be attained during the non-oxidative dissolution of a nickel matte. In fact, better separation of nickel and copper can be obtained in an atmosphere containing hydrogen sulphide.

When iron powder was added to the reaction mixture, there was an initial cathodic shift in the mixed potential of the leach. However, the iron dissolved rapidly, with

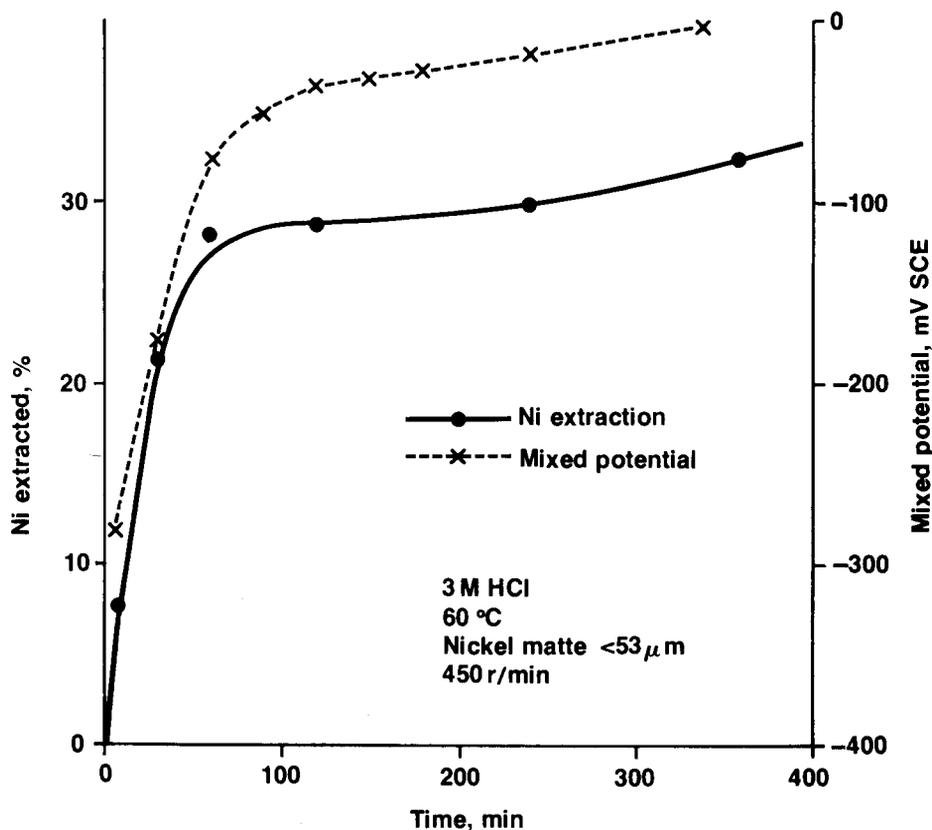


Fig. 10—Leaching of high-grade matte with 2g of sulphur

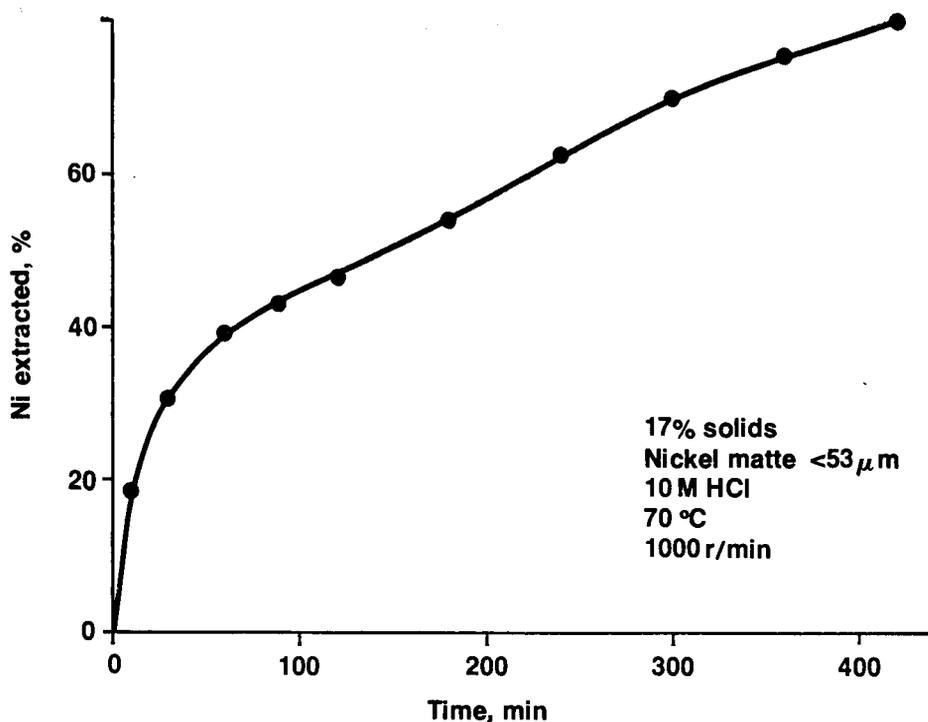


Fig. 11—Nickel extraction from high-grade matte at high pulp density

a resulting anodic shift in potential, and had little effect on the rate of nickel dissolution.

The effect of the addition of 2 g of sulphur to the slurry is shown in detail in Fig. 10. Initially, the reaction was fast, but, after 30 per cent of the nickel had been extracted, the dissolution virtually ceased. The rate of nickel dissolution is closely related to the mixed potential of the slurry during the reaction, which was initially about -350mV , and shifted anodically to about -50mV . The addition of sulphur therefore shifts the potential anodically: initially to a potential where nickel dissolution is fast (Table II), and then further anodically where the rate of non-oxidative dissolution is slow. This slow reaction corresponds to the behaviour of synthetic nickel sulphides that are deficient in nickel, since these materials dissolved very slowly at anodic mixed potentials⁴. It appears likely that the sulphur is reacting with dissolved hydrogen sulphide to form polysulphides that are subsequently reduced at the matte surface, thus shifting the mixed potential of the nickel matte anodi-

TABLE VII

EFFECT OF ADDITIVES ON THE LEACHING OF NICKEL MATTE

Conditions	Potential mV(SCE)	$k_{\text{Ni}} \times 10^3$, mol.cm ⁻² .s ^{-1/2}
Standard*	-330	7,8
+2g of S	-280 → +10	13,7†
+0,1g of S	-280	10,9
+2g of Fe	-400 → -310	8,8
+H ₂ S bubbled through solution	-330	7,9

*3M hydrochloric acid, 60°C, stirring at 450 r/min, matte < 53μm, 3% solids.

†Calculated from the first three points of Fig. 7.

TABLE VIII

RESULTS FOR THE LEACH CONDUCTED AT HIGH PULP DENSITY
Conditions: 10M hydrochloric acid, 70°C, 11h, 17% (by mass)
solids, nickel matte < 53μm

Element	Ni	Cu	Co	Fe	S	Pt	Pd	Au	Rh
% leached	89	2	95	90	56	70	50	65	70

cally. A small amount of sulphur (0,1 g) added to the reaction medium resulted in a shift in mixed potential to a constant value of -280mV and an increase in the rate of nickel dissolution throughout the duration of the reaction. Thus, a small amount of sulphur added to the slurry has an overall beneficial effect on the non-oxidative dissolution of nickel matte, but the reaction is retarded if the amount added is such that it causes the mixed potential to shift to a value that is anodic of the optimum. It is therefore apparent that the addition of oxidants to a leach alters the reaction rate in the manner predicted from electrochemical studies. The effect of a sulphur barrier, which has been found to inhibit the dissolution of nickeliferous pyrrhotite⁷, probably results from a similar anodic shift in mixed potential to a value at which non-oxidative dissolution is slow.

A process-oriented leach was designed that allowed for the effect of variables on the rate of non-oxidative dissolution of nickel. The Falconbridge matte-leaching process¹ was also borne in mind. Acid concentration and temperature were considered to be the two most important variables in the design of the reaction. The conditions under which the leach was carried out and the resulting nickel-dissolution curve are shown in Fig. 11. Table VIII shows the metals extracted from the

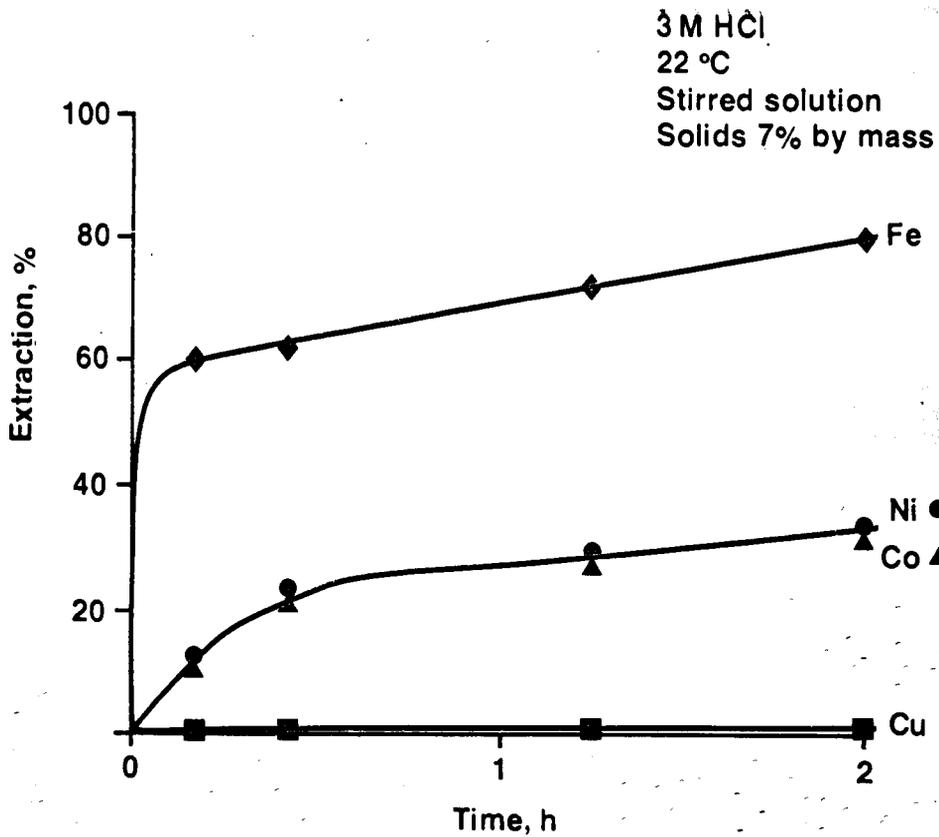


Fig. 12—Rate of dissolution of low-grade matte

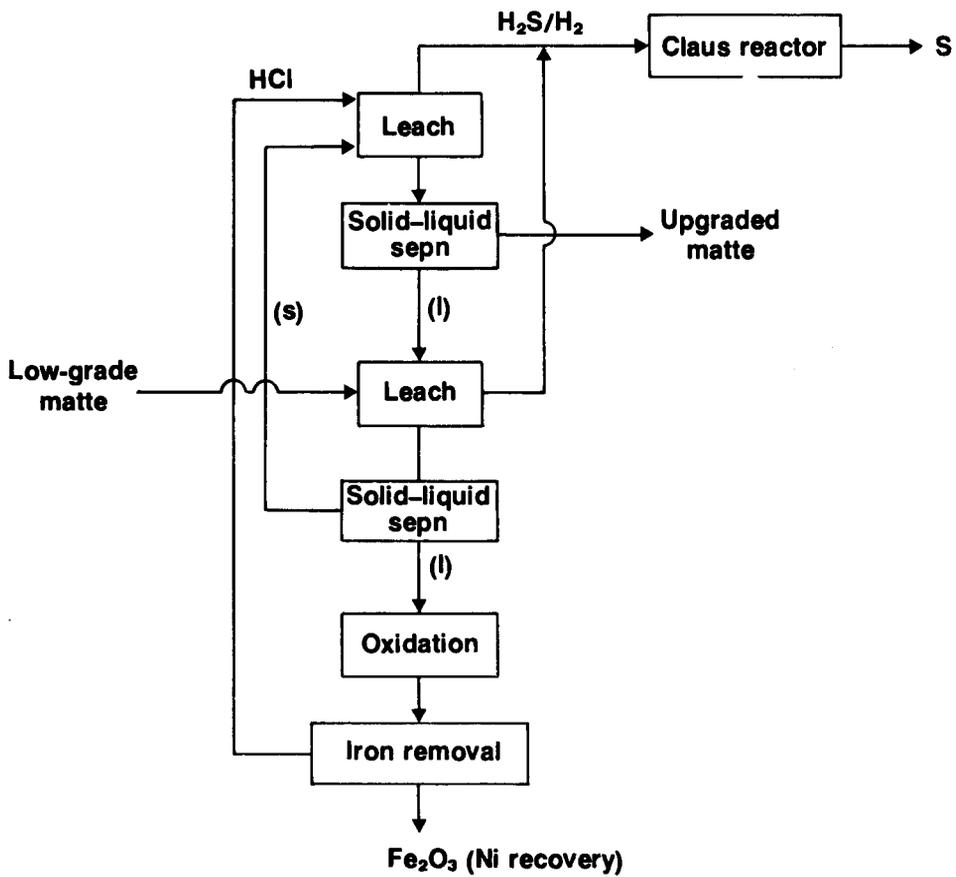


Fig. 13—A flowsheet for the upgrading of low-grade matte

matte during the leach. The overall rate of nickel extraction was not as fast as that reported for the Falconbridge process¹, and significant amounts of the precious metals were dissolved. The latter observation is not in agreement with results reported previously^{1, 8} or with theoretical expectations.

Owing to poor reproducibility due to the sampling and analytical procedures, the values for the extraction of the precious metals cannot be regarded as accurate, but they do show that the precious metals were extracted partially. It seems likely that this dissolution was due to an oxidative rather than a non-oxidative process. One of the principal advantages of a non-oxidative dissolution process is the separation of values in the leaching stage. The dissolution of precious metals, as indicated by Table VIII, is therefore a major drawback to the implementation of such a process.

Dissolution of Powdered Low-grade Matte

A 25g sample of low-grade matte smaller than 100 mesh was dissolved in 350 ml of 3M hydrochloric acid at 22°C. The dissolution rates of iron, nickel, copper, and cobalt are shown in Fig. 12. The potential measured at a platinum-plate electrode shifted from -300 to -350 mV during the reaction. Iron was leached much more rapidly than nickel or cobalt, particularly at the beginning of the reaction, and copper was not extracted. Gas was evolved vigorously during the reaction. A residue containing 27 per cent iron, 19 per cent nickel, 30 per cent copper, 1.7 per cent cobalt, and 18.6 per cent sulphur was produced. The initial separation of iron from nickel in the leaching stage was good, but, in the extraction of a large proportion of the iron, significant extractions of nickel were inevitable. Treatment of the pregnant solution with fresh matte resulted in the precipitation of some nickel and cobalt and the dissolution of further iron. This probably reflects reactions like $Ni^{2+} + FeS \rightarrow Fe^{2+} + NiS$. A possible flowsheet for an upgrading process based on these results is given in Fig. 13. The treatment of a low-grade matte in this way may be desirable if the matte is to be transported before being refined further. A pregnant solution (iron 68 g/l, nickel 5.4 g/l, cobalt 0.3 g/l and copper 1 p.p.m. at a pH value of 0.3) and a solid (iron 26 per cent, nickel 21 per cent, copper 31 per cent, cobalt 2 per cent and sulphur 19 per cent) were obtained by such a two-stage leaching technique. A similar process can be envisaged in sulphate media, the iron being removed and the sulphuric acid regenerated by high-temperature hydrolysis.

Complete dissolution of nickel, cobalt, and iron from the low-grade matte to leave a copper sulphide precipitate is also possible. The reactivity of nickel sulphide is lower than that of iron sulphide, and either a longer reaction time or a higher reaction temperature is therefore needed to give complete dissolution of both the

nickel and the iron. When 20 g of low-grade matte was dissolved in 300 ml of 3M hydrochloric acid at 60°C for 18 hours, the percentage extractions, determined from analyses of the residue, were as follows: nickel 83 per cent, cobalt 89 per cent, iron 94 per cent, copper 1 per cent or less, and sulphur 73 per cent. The residual sulphide had a copper content of 35 per cent.

Conclusions

The dissolution rates of nickel and hydrogen sulphide from a high-grade nickel matte, and of nickel and iron from a low-grade nickel matte, were found to depend on the potential at which the reaction occurs. This potential is a function of the stoichiometric ratio of nickel to sulphur at the reaction surface, and can be adjusted by the addition of redox reagents or by the direct application of potentials.

The leaching of powdered high-grade matte was found to depend on the concentration of the acid, and exhibited an activation energy of 40 kJ.mol⁻¹. The nickel and copper present can be separated by a non-oxidative leaching process. A small amount of sulphur added to the slurry enhances the dissolution rate of the nickel matte, but greater quantities of sulphur 'poison' the reaction. The leaching of low-grade matte resulted in a reasonable separation of iron from nickel and copper. The rate of dissolution of both mattes is satisfactory for non-oxidative processing of the materials, provided that there are procedures for the recovery of the other constituents as impurities in the subsequent refining of the individual components.

Acknowledgements

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