EXTRACTION OF NICKEL AND COBALT WITH 2-ETHYLHEXYLPHOSPHONIC ACID MONO-2-ETHYLHEXYL ESTER

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Extraction equilibrium formulations were established for the distribution of nickel, cobalt and sodium between n-heptane and xylene containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester ((LH)2) and 5 x 10^2 mol/m^3 (Na, H)NO₃. The composition of the organic phase species is NiL₂(LH)₂, CoL₂(LH)₂ and NaL(3/2)(LH)₂, over a range of loading ratio, [ML]/[(LH)₂]_feed, less than 0.08 for cobalt and 0.008 for nickel. The ratio of the extraction constant for the commonly used di-(2-ethylhexyl)phosphoric acid to that using the present reagent is of the order of 10 for cobalt, copper and sodium, but increases to the order of 100 for nickel.

With increase in loading ratio, successively larger aggregated species such as (NiL₂(LH)₂)ₙ(LH)₂ and (CoL₂)ₙ(LH)₂ (n = 1, 2, 3, ···) appear. Identification of these species has been established on the assumption that the extraction constants are independent of the number of metal atoms, n, in the species.

Introduction

Since the successful commercial application of hydroxyoxime chelating extractants for copper recovery from acidic leach liquor in the mid-1960s, the liquid-liquid extraction of metals has gained increasing importance in general hydrometallurgical processing as well as in nuclear fuel reprocessing. The metal which excites most interest after copper is probably nickel, and a number of investigations have been published for the extraction of nickel and its separation from cobalt. These were reviewed and discussed by Flett and Spink,7) Murayama19) and Warshawsky.29)

For the separation of nickel and cobalt, there are two processes, one using chloride solution and the other an acidic sulphate or nitrate solution. In the first case, cobalt is extracted, with the nickel being retained in the raffinate, using a long-chain alkylamine in a concentrated solution of chloride. Only cobalt is able to form a stable anionic chlorocomplex, and this enables the separation to be satisfactorily achieved. In the second case, acidic reagents and chelating reagents have been proposed as possible extractants, for example carboxylic acid,6'16) dioximes,4) hydroxyoximes,24) a mixture of hydroxyoxime and carboxylic acid,8) dialkylphosphorodithionic acid.26) Di-(2-ethylhexyl)phosphoric acid11,25) has been regarded as the most potential reagent until recently. Pilot-scale tests have been performed, using di-(2-ethylhexyl)phosphoric acid (abbreviated as HDEHP), and the applicability of this process to plant-scale operation illustrated. The extraction characteristics, however, are not satisfactory, so that it was necessary to have a multi-stage extraction process, including several scrubbing stages, for satisfactory separation. Consequently, none of these reagents has been able to demonstrate promising characteristics for the separation of nickel and cobalt, as pointed out by Flett and Spink.7)

Recently, alkylphosphonic acid monoester, especially 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (abbreviated as EHPNA or simply LH) has been found to be a prospective reagent for the separation of nickel and cobalt.9) A new process for winning high-purity nickel and cobalt, depending for its successful operation on this new extractant, has also been exploited.13) This reagent has also been found to have better features than HDEHP for the separation of rare-earth elements,5'10) and for the separation of copper and zinc.20) It should be noted that it is not a novel reagent as an extractant for metals, since studies were reported for thorium extraction in 1962,23) and for the state of dimerization in the organic phase in 1961.22)

A systematic study of the equilibrium formulation of each metal, diluent and modifier effect, separation factor for the metals and the kinetic behaviour is needed in order to obtain a reasonably complete picture of the separation and purification of the metals in this extraction system. In addition, information about high fractional conversion of the reagent to the metal complex is also required to achieve the practical commercial operating conditions. In the present work, as a first step, measurements have been made of the extraction equilibrium performance for nickel, cobalt and sodium. The mechanism of the extraction system can then be deduced and compared with that of the previous HDEHP extraction system.15) The range of conversion of the extractant to
1. Experiments

1.1 Reagents

The reagent, EHPNA, kindly supplied by Daihachi Chemicals Ind. Co., Ltd., Japan, having a purity of 95%, was further purified by precipitation as a copper complex from ether solution, following the procedure developed for purification of HDEHP by Partridge and Jensen. All inorganic chemicals and the diluents, n-heptane and xylene, were supplied by Wako Chemical Ltd. as analytically pure reagent grade. n-Heptane and water were purified by simple distillation.

The aqueous metal nitrate solutions were prepared by dissolving metal nitrate in distilled water, to which $5 \times 10^{-2}$ mol/m$^3$ (Na, H)NO$_3$ had been added. The organic solutions were prepared by diluting EHPNA in a diluent.

1.2 Procedure

Organic solutions and aqueous solutions having volume ratios 1:1 or 2:1 were equilibrated at 25$\pm$0.1°C. A weighed organic sample was stripped with 20wt% nitric acid and the resulting aqueous sample analyzed for nickel, cobalt, or sodium at an appropriate wave number using a Jarrell Ash 702 atomic absorption and emission spectrophotometer. The aqueous-phase pH value was measured with an Orion 601 pH meter equipped with a 91-01 glass electrode and a 90-02 calomel electrode.

It has been shown by a vapour-phase osmometric study and by a similar technique that the majority of molecules are dimerized in nonpolar diluents. The concentrations of dimeric species are therefore used in the present work. The concentrations of dimeric species were evaluated simply by determining 
\[
[(LH)_2]^\text{feed} - a \cdot [M]_f,
\]
where $a$ is the number of dimeric EHPNA molecules involved in the metal complex. In the majority of cases, however, the concentration change was negligible, since the loading ratio of the organic phase, $[M]_f/[(LH)_2]^\text{feed}$, was kept less than 0.002.

Assuming that nickel and cobalt cations are extracted as a $j$-merized complex of the composition, $(ML_2(LH)_2)_j$, into the organic phase, the extraction equilibrium can be described by the general equation
\[
jM^{2+} + (j+x+1)(LH)_2 \rightleftharpoons (ML_2(LH)_2)_j + 2H^+.
\]

The distribution ratio of metal is given by
\[
D_M = \frac{\bar{C}_M}{C_M} = \frac{j[(ML_2(LH)_2)_j]}{[M^{2+}]},
\]
which leads to
\[
\frac{\bar{C}_M}{C_M} = jK_{ex}[M^{2+}]^{j+x+1}/[H^+]^2.
\]

The slope of the plot of $\bar{C}_M$ against $[M^{2+}]/[H^+]^2$ at constant concentrations of EHPNA in the diluent gives the degree of association of the metal–EHPNA complex in the organic phase. The results are plotted in Fig. 1. Straight lines of slope 1 are obtained for both metals. The extracted species is therefore monomeric. The distribution ratio can then be simplified to
\[
D_M = K_{ex}[(LH)_2]^{x+1}/[H^+]^2.
\]

The variation of $D_M[H^+]^2$ with $[(LH)_2]$ is shown in Fig. 2. For cobalt, straight lines of slope 2 are obtained, indicating that the composition is $\text{CoL}_2(LH)_2$. For nickel, straight lines of slope 3 are obtained, indicating that the species is $\text{NiL}_2(LH)_2$. The overall extraction equilibria may be formulated as follows.

\[
\begin{align*}
\text{Co}^{2+} + 2(LH)_2 & \rightleftharpoons \text{CoL}_2(LH)_2 + 2H^+ \quad (4) \\
\text{Ni}^{2+} + 3(LH)_2 & \rightleftharpoons \text{NiL}_2(LH)_2 + 2H^+ \quad (5)
\end{align*}
\]

These equations are identical to those obtained in the HDEHP extraction system, with different extraction equilibrium constants. The extraction constants are summarized in Table 1, together with published data.

Several series of runs have been made, where equilibrium organic-phase metal concentration has been varied. The apparent extraction constants obtained on the basis of Eqs. (4) and (5) are plotted against loading ratio in Fig. 3. The values remain constant up to 0.08 for cobalt and 0.008 for nickel, indicating that single species, $\text{CoL}_2(LH)_2$ and $\text{NiL}_2(LH)_2$, respectively, exist over the range of loading ratio less than 0.08 and 0.008.

2.2 Extraction equilibria for high loading of the organic phase

An increase in the loading ratio of the organic phase is achieved by raising the aqueous-phase pH.
levels. For pH values greater than 6.0, which are near the limit at which the metal hydroxide is precipitated, some experimental values of the ratio, $[M]/[(LH)_2]_{diss}$, were found to exceed 1.0. This is not possible if the organic metal compounds are formed entirely from EHPNA to give, for example $(CoL_2)_n$ or $(NiL_2)_n$. Some hydroxylated metal species or others containing NO$_3^-$ group might also be extracted into the organic phase. For simplicity, however, the data considered here were taken in the range of pH less than 5.5 for cobalt and 5.7 for nickel.

A sharp increase in the apparent extraction constant is shown in Fig. 3 and may suggest that the number of free dimeric EHPNA molecules associated with each metal starts to decrease below 1 for cobalt and 2 for nickel. To estimate the concentration of EHPNA at extraction equilibrium conditions, the molecular form, or at least the stoichiometric relation between metal and EHPNA, is needed. The formation of successively larger aggregated species in the organic phase can now be considered. For cobalt, the typical steps are:

$$\text{Co}^{2+} + 2(LH)_2 \rightleftharpoons \text{CoL}_2(LH)_2 + 2H^+$$

$$K_{ex,Co} = \frac{[\text{CoL}_2(LH)_2][H^+]^2}{[\text{Co}^{2+}][\text{LH}_2]^2}$$

$$\text{Co}^{2+} + \text{CoL}_2(LH)_2 + (LH)_2 \rightleftharpoons (\text{CoL}_2)_2(LH)_2 + 2H^+$$

$$K_{Co,2} = \frac{[(\text{CoL}_2)_2(LH)_2][H^+]^2}{[\text{Co}^{2+}][\text{CoL}_2(LH)_2][\text{LH}_2]^2}$$

$$\text{Co}^{2+} + (\text{CoL}_2)_{n-1}(LH)_2 + (LH)_2 \rightleftharpoons (\text{CoL}_2)_n(LH)_2 + 2H^+$$

$$K_{Co,n} = \frac{[(\text{CoL}_2)_n(LH)_2][H^+]^2}{[\text{Co}^{2+}][(\text{CoL}_2)_{n-1}(LH)_2][\text{LH}_2]^2}$$

The assumption that the value of $K_{Co,n}$ (except when $K_{Co,1} = K_{ex,Co}$) is independent of $n$ is used, which means that the ratios of concentrations of successively larger metal-EHPNA complexes, $\gamma$, are constant for all species, i.e.

$$K_{Co,p} = K_{Co,2} = K_{Co,3} = \cdots = K_{Co,n} = \frac{\gamma[H^+]^2}{[\text{Co}^{2+}][\text{LH}_2]^2}$$

where

$$\gamma = \frac{[(\text{CoL}_2)_2(LH)_2]}{[\text{CoL}_2(LH)_2]} = \frac{[(\text{CoL}_2)_3(LH)_2]}{[(\text{CoL}_2)_2(LH)_2]} = \cdots = \frac{[(\text{CoL}_2)_n(LH)_2]}{[(\text{CoL}_2)_{n-1}(LH)_2]}$$

This assumption was first introduced in the analysis of uranium extraction with HDEHP by Bayes et al., and later for cobalt extraction with HDEHP by Brisk.
Table 1. Extraction constants using EHPNA and HDEHP

<table>
<thead>
<tr>
<th>Metal</th>
<th>Aqueous phase</th>
<th>HDEHP</th>
<th>EHNPA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sources</td>
<td>$K_{ex}$</td>
<td>Sources</td>
</tr>
<tr>
<td>Co</td>
<td>$0.5 \text{ M (Na, H)}\text{NO}_3$</td>
<td>$n$-Heptane</td>
<td>$4.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>Cu</td>
<td>$0.1 \text{ M (Na, H)}\text{Ac}$</td>
<td>$n$-Heptane</td>
<td>$9.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>Ni</td>
<td>$0.1 \text{ M (Na, H)}\text{SO}_4$</td>
<td>$n$-Heptane</td>
<td>$4.5 \times 10^{-8}$</td>
</tr>
<tr>
<td>Na</td>
<td>$0.5 \text{ M (Na, H)}\text{NO}_3$</td>
<td>$n$-Heptane</td>
<td>$4.0 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>$(\text{Na, H})\text{NO}_3$</td>
<td>Benzene</td>
<td>$3.0 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$0.5 \text{ M (Na, H)}\text{ClO}_4$</td>
<td>$n$-Heptane</td>
<td>$5.5 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

and McManamey.\(^3\)

The total concentration of cobalt in the organic phase is expressed as

$$[\text{Co}]_t = [\text{CoL}_2(\text{LH})_2](1 + 2\gamma + 3\gamma^2 + \cdots + n\gamma^{n-1})$$

The total concentration of EHPNA bound in the metal complex can then be expressed as

$$[(\text{LH})_2]_{\text{in complex}} = (2 - \gamma)[\text{Co}]_t$$

Combining Eqs. (4), (9) and (10) gives

$$K_{ex,\text{Co}} = \frac{(1 - \gamma)^2[\text{Co}]_t[\text{H}^+]^2}{[\text{Co}^2+][((\text{LH})_2)_{\text{feed}} - (2 - \gamma)[\text{Co}]_t]^2}$$

Using Eq. (11), $\gamma$ is expressed directly in terms of measured values by

$$\gamma = \frac{2[\text{Co}]_t - [(\text{LH})_2]_{\text{feed}} + [\text{Co}]_t[\text{H}^+]^2/[\text{Co}^2+][K_{ex,\text{Co}}]^{1/2}}{[\text{Co}]_t + [(\text{LH})_2][\text{H}^+]^2/[\text{Co}^2+][K_{ex,\text{Co}}]^{1/2}}$$

For nickel, the typical steps are:

$$\text{Ni}^{2+} + 3(\text{LH})_2 \rightleftharpoons \text{NiL}_2(\text{LH})_2 + 2\text{H}^+$$

Using Eqs. (4), (9) and (10) gives

$$\gamma = \frac{2\text{[Ni]}_t - [(\text{LH})_2]_{\text{feed}} + \text{[Ni]}_t[\text{H}^+]^2/[\text{Ni}^2+][((\text{LH})_2)_{\text{feed}} - (2 - \gamma)[\text{Ni}]_t]^2}{\text{[Ni]}_t + [(\text{LH})_2][\text{H}^+]^2/[\text{Ni}^2+][K_{ex,\text{Ni}}]^{1/2}}$$

The values of $K_{ex,\text{Co}}$ and $K_{ex,\text{Ni}}$ obtained from Eqs.
Fig. 4. Extraction constants for aggregated organic compound obtained using Eqs. (12), (17) and (18).

(8), (10) and (12) and Eqs. (17) and (18) are plotted against the loading ratios in Fig. 4. Both values show considerable scatter. Some error in the measurement is inherently contained in the data and small variations in the total organic metal concentration have a great effect on the computed values of $K_{Co,p}$ and $K_{Ni,p}$.

An alternative approach using least square parameter estimation can also be used. Following usual procedure the squares of the residuals are introduced as follows.

For cobalt,

$$f_1 = (K_{ex,Co,a} - K_{Co,p,a})^2 + (K_{Co,p,a} - K_{Co,p})^2$$

$$= \left( K_{ex,Co,a} - \frac{(1 - \gamma)[Co][H^+]{(2 - \gamma)[Co]}^2}{[Co^{2+}] \left( [(LH)_{2}]_{feed} - (2 - \gamma)[Co] \right)^2} \right)^2 + \left( K_{Co,p,a} - \frac{\gamma[H^+]}{[Co^{2+}] \left( [(LH)_{2}]_{feed} - (2 - \gamma)[Co] \right)^2} \right)^2$$

and for nickel,

$$f_2 = (K_{ex,Ni,a} - K_{Ni,p,a})^2 + (K_{Ni,p,a} - K_{Ni,p})^2$$

$$= \left( K_{ex,Ni,a} - \frac{(1 - \gamma)[Ni][H^+]{(3 - \gamma)[Ni]}^2}{[Ni^{2+}] \left( [(LH)_{2}]_{feed} - (3 - \gamma)[Ni] \right)^2} \right)^2 + \left( K_{Ni,p,a} - \frac{\gamma[H^+]}{[Ni^{2+}] \left( [(LH)_{2}]_{feed} - (3 - \gamma)[Ni] \right)^2} \right)^2$$

where constants with subscript $a$ are the maximum likelihood values of the constants. For constants of the monomeric species, the values determined in the measurement of the equilibrium data at very low loading ratio shown in Fig. 2 have been used as $K_{ex,Co,a} = 7.53 \times 10^{-7}$ and $K_{ex,Ni,a} = 1.50 \times 10^{-11}$ mol/m$^3$. The values of $K_{Co,p,a}$ and $K_{Ni,p,a}$ were then determined so as to minimize the sum of squares of residual for all runs. The values thus determined are $K_{Co,p,a} = 1.5 \times 10^{-7}$ and $K_{Ni,p,a} = 1.5 \times 10^{-10}$ mol/m$^3$ for xylene diluent. From this the value of $\gamma$ in each run can then be calculated, enabling the EHPNA concentration at equilibrium conditions to be determined.

The results are plotted for cobalt in Figs. 5 (a) and (b), and for nickel in Figs. 6 (a) and (b). All data fall on the corresponding straight lines. Values of $\gamma$ are plotted against the loading ratio in Fig. 7. For nickel species $\gamma$ increases more sharply than for cobalt. The behaviour of the metal–EHPNA complex at high loading ratios of the organic phase can be obtained from the simple scheme proposed.

2.3 Extraction equilibrium of sodium

All the working solutions of the aqueous phase contained 5 x 10$^2$ mol/m$^3$ sodium nitrate. When the amount of sodium extracted into the organic phase is not negligible compared with that of nickel or cobalt, the change of concentration of EHPNA due to sodium extraction should be taken into account. All the data are plotted in Fig. 8 as $D_{Na}[H^+]$ against the EHPNA concentration. Although there is considerable scatter, no significant difference can be seen between the data for sodium extraction from a single solution of sodium and those from a solution of binary metals of sodium with nickel or cobalt. This
indicates the absence of interaction between sodium and nickel or cobalt which may influence the amount of each of the metals extracted. Consequently, the extraction equilibrium relation is expressed as

\[
\text{Na}^+ + 2(\text{LH})_2 \rightleftharpoons \text{NaL}(3/2)(\text{LH})_2 + \text{H}^+ 
\]

This formulation is identical to that obtained with HDEHP. The extraction constant is shown in Table 1, together with some published results for HDEHP.

The amounts of nickel, cobalt and sodium extracted into the organic phase are calculated and compared for each run. Cobalt extraction is about two orders of magnitude greater than that of sodium for all runs under the present experimental conditions. The ratio of the amount of nickel extracted to that of sodium is about six at a pH of around 5, and this ratio increases to twenty at a pH of around 5.6. The majority of runs for the high loading ratio of organic phase were carried out at these relatively high pH levels. The contribution of sodium extraction from the reduction in free EHPNA concentration was therefore discounted.

3. Discussion

3.1 Relation of metal extracted to hydrogen ion liberated

According to the scheme given by Eqs. (7) and (14), twice as many hydrogen ions as the metal extracted will be liberated. This increase in hydrogen ion concentration is determined by the difference in pH values of the feed solution and the equilibrated solution, and by the amount of sodium hydroxide which must be added to the feed solution. The results are plotted in Fig. 9. In the case of cobalt extraction, all the data fall on the diagonal line of slope 1. In the case of nickel, however, the resulting hydrogen ion concentration is twice that represented by the nickel extracted at low nickel values. The difference becomes less as the amount of nickel extracted increases. Taking account of the effect of sodium extraction, the difference is only 10–20% smaller. It is possibly that the aqueous distribution of the EHPNA and succeed-
ing acid dissociation may cause the difference, since the data were taken at pH values of 5-5.7.

3.2 Comparison of extraction equilibrium compositions and efficiency of EHPNA and HDEHP

The overall extract compositions for cobalt, nickel and sodium with EHPNA are found to be identical to those obtained for HDEHP. In addition, the extract compositions obtained for copper,20) zinc20) and lanthanides5) with EHPNA have also been found to be the same as those when HDEHP is used.14,18,27) Extraction constants for cobalt, nickel, copper, and sodium are tabulated in Table 1. The pH-functionality of EHPNA is generally lower than that for HDEHP. The ratio of the constant, \( K_{ex,Co}/K_{ex,Ni} \), obtained with EHPNA is 1.4 x 10^4 to 5.0 x 10^4 mol/m^3, while that with HDEHP is 8.9 x 10^2 to 3.0 x 10^3 mol/m^3. This explains why EHPNA is better for the separation of nickel and cobalt.

Conclusion

1. The overall extraction equilibrium equations for cobalt and nickel with EHPNA are expressed by Eqs. (4) and (5), and thus the extracted species are \( \text{CoL}_2(\text{LH})_2 \) and \( \text{NiL}_2(\text{LH})_2 \), indicating that they are identical to those obtained with HDEHP. These hold for loading ratios of the organic phase less than 0.08 for cobalt and 0.008 for nickel. The equilibrium equation for sodium is expressed by Eq. (21) where the complex is \( \text{NaL}(3/2)(\text{LH})_2 \). The resulting extraction constants for these metals are tabulated in Table 1, together with the published data for HDEHP. Ratios of the extraction constants for HDEHP to those for EHPNA used here are of the order of 10 for cobalt, copper and sodium, but increase to the order of 100 for nickel.

2. With increase in loading ratio of the organic phase, successively larger aggregated metal–EHPNA species appear. The equilibrium equations are expressed with Eqs. (7) and (14) and the equilibrium constants are found to be determined as \( K_{Co,p} = 1.5 \times 10^{-7} \) and \( K_{Ni,p} = 1.5 \times 10^{-10} \) mol for xylene diluent. These equations hold up to the high loading ratios that would represent conditions of practical importance for the separation of nickel and cobalt.

Nomenclature

\( C \) = concentration [mol/m^3]
\( D \) = distribution ratio [--]
\( f \) = square of residual of predicted and observed constants
\( K_{ex} \) = extraction constant for monomeric metal species defined by Eqs. (4) and (5)
\( K_p \) = extraction constant for aggregated metal species defined by Eqs. (7) and (14)
\( y \) = ratio of concentrations of successively larger metal–EHPNA aggregated species

\( \text{feed} \) = initial or feed value
\( (\text{LH})_2 \) = extractant, EHPNA
\( M \) = metal
\( n \) = number of metal atoms in metal–EHPNA aggregated species

Literature Cited

KINETIC STUDY OF OXIDATION OF PELLETED ZINC SULFIDE POWDER HAVING GRAIN SIZE DISTRIBUTION

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Oxidation of porous zinc sulfide pellets, composed of fine grains having log-normal size distributions, was carried out using a differential flow reactor under oxygen partial pressure of 1-16 kPa and temperature of 953-1113 K.

The overall conversion rate data were represented by a simple power law rate expression. The reaction order with respect to the solid reactant varied with the standard deviation of the grain size distribution. This variation agreed well with the theoretical prediction by the grain model accounting for grain size distribution. The reaction order with respect to the gaseous reactant was 1/2.

The surface rate constant was then found to be correlated in an Arrhenius equation.

$k' = 5.56 \times 10^9 e^{-244/RT} \text{ (mol}^{1/2}/\text{m}^{1/2}\text{s)}$

The rate constant agreed well with that for oxidation of sphalerite single crystals by other workers as well as with the rate constant reproduced from the data in the literature on oxidation of porous pelleted zinc sulfide.

Introduction

Gas-solid reactions involving a porous solid are numerous and industrially of great importance. For the interpretation and application of rate data observed in a variety of gas-solid reactions a number of kinetic models have been proposed.

It has been known that the kinetics by which the reaction proceeds depends entirely on the structure of the solid phase. The kinetic model describing the data is therefore required to reflect somehow the actual structure of the solid. In this light, the grain model may be noteworthy for its simple but practical microscopic structural representation. This model assumes that the porous solid is an ensemble of grains of uniform size. A gaseous reactant diffuses through pores between grains and reacts on the unreacted core formed in each grain.

The grain model is expected to be especially applicable when a pellet involved in the reaction is molded using powdered solid reactant by hand rolling, compression, sintering, etc. In the usual situation, however, the grains of the powdered reactant are considered not to be uniform in size but rather to have a size distribution. In such cases the model assuming uniform grain size may not be properly applied. Several workers have predicted by numerical calculation the influence exerted upon the gross behavior by the grain size distribution. Although they pointed out the differences from the model assuming uniform grains, it was not very simple to apply their results to practical situations.

In this work the oxidation of pelleted zinc sulfide powder is investigated in detail. The rate data are analyzed on the basis of a simple rate equation derived from a grain model accounting for the grain...