

地下水水質形成モデル開発のための 鉍物溶解速度データの整備

(動力炉・核燃料開発事業団 研究概要)

1995年2月

三菱マテリアル株式会社

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地下水水質形成モデル開発のための 鉍物溶解速度データの整備

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田中 皓*

要 旨

地下水生成モデルの研究において必要な鉱物の溶解速度について研究を行った。
成果概要を以下にまとめる。

1. 鉱物の溶解速度データの調査

溶解速度データが整備されていない黄鉄鉱、緑泥石、緑簾石、菱鉄鉱の4種類の鉱物についてDIALOGによる文献調査を実施した。成果の概要を以下にまとめる。

(1) 黄鉄鉱

Lin らにより、酸素濃度による反応速度定数 k が定義されている。

$$1 - (1 - x)^{1/3} = k [O_2]^{1/2} \cdot t$$

(x : 反応したFeS のモル数、 $[O_2]$: 溶存酸素濃度、 t : 時間)

また、その温度依存性について $k = 2.2 \times 10^9 \exp(-9140/T)$ を示している。

pHによる影響についてはCiminelli らにより、溶解中性～アルカリ性で黄鉄鉱の溶解速度はpHとほぼ線型に増加することが示されている。

(2) 緑泥石

Swoboda-Colberg らにより、 $2.7 \sim 6.7 \times 10^{-12} \text{ mol/m}^2/\text{s}$ (pH3~4.5)の値が示されている。また、Rossらにより溶解反応のメカニズムは拡散律速であり、陽イオンの溶解量に化学量論的な関係があることが示されている。

(3) 緑簾石

Roseにより、pH 1~11において $10^{-14} \sim 10^{-13} \text{ mol/cm}^2/\text{s}$ の値が示されている。

(4) 菱鉄鉱

Greenberg らにより、脱酸素水中において $9.93 \times 10^{-6} \text{ mol/m}^2/\text{s}$ の値が示されている。

2. 鉱物-水反応試験による反応速度データの取得

(1) 黄鉄鉱

還元雰囲気及び大気平衡状態の蒸留水中における黄鉄鉱の溶解速度を測定した。

Lin らの式に従って、大気平衡の蒸留水中での溶解速度定数 k を評価した結果、 $10^{-4} \sim 10^{-3} (\text{cm}^3 \cdot \text{mol}^{-1})^{1/2} \cdot \text{h}^{-1}$ と評価された。

(2) 緑泥石

蒸留水中での緑泥石の溶解速度を測定した。溶解は放物線溶出反応にあることが確認された。Rossらの式に従って、溶解速度定数 k を評価した結果、 $10^{-15} \sim 10^{-14}$ の範囲であった。

$$\alpha^2 = k t$$

(α : 溶解した鉱物量と初期存在量の比、 t : 時間)

本報告書は、三菱マテリアル株式会社が動力炉・核燃料開発事業団の委託により実施した研究の成果である。

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第1章 鉱物の溶解速度データの調査

1.1 調査の概要

1.1.1 対象鉱物

溶解速度データの調査を行った鉱物は以下の4種類である。

- ①黄鉄鉱 (pyrite, iron pyrite)
- ②緑泥石 (chlorite)
- ③緑簾石 (epidote)
- ④菱鉄鉱 (siderite)

1.1.2 データベースの状況

文献調査では、DIALOGを使用した。検索に際し、用いたキーワードは次の通りである。

(鉱物名称) × (DISSOLUTION+LEACHING) × (RATE+KINETIC)

検索の結果、表1.1.1 に示す件数の文献が検索された。これらのうちから、溶解速度データに関連していると思われる文献をさらに抽出して文献調査の対象とした。

Table 1.1.1 The number of references researched in DIALOG database

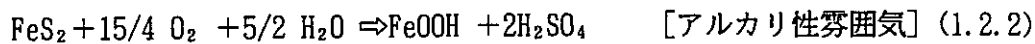
database	minerals			
	pyrite	chlorite	epidote	siderite
CA SEARCH	149	14	1	2
GEOREF	5	4	1	4

1.2 黄鉄鉱

黄鉄鉱 (pyrite) の溶解速度の調査結果を表1.2.1 にまとめて示す。

1.2.1 溶解反応

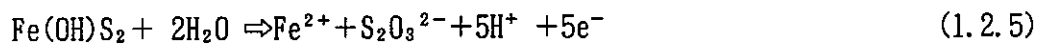
黄鉄鉱 (FeS_2) の溶解反応はCiminelli ら¹⁾により、次のように示されている。



また、Osseo-Asare²⁾ は水との反応として次の反応を示している。



これは FeS_2 表面の変化であり、さらに溶解反応として次の反応を示している。



1.2.2 溶解速度式

Lin ら³⁾らは、 O_2 共存下での溶解速度式として次の式を示している。反応速度 k は、実験データを $1 - (1-X)^{1/3}$ と $[\text{O}_2]^{1/2} t$ で整理することによって求められる。

$$1 - (1-X)^{1/3} = k [\text{O}_2]^{1/2} t \quad (1.2.7)$$

X : 反応した FeS_2 のモル数
[O_2] : 溶存酸素濃度
t : 反応時間
k : 反応速度定数

Table 1.2.1 Data base of leaching rate for pyrite

Author	Year	The place of origin	Pre-treatment	Solution pH	Surface area	Solution	Solid solution ratio	Temperature	Filteration	Shaking	Leaching rate
T. Nagai	1968	Sasatani mine, Uku mine, Wagasennin mine, Washiai mine	no-discribed	no-discribed	no-discribed	1N H ₂ SO ₄	25cm ² /450ml	115 ~175 °C	no-discribed	0 ~800 rpm	0.1 ~10mg-Fe/cm ² /h
R. S. Schechter	1984	Combustion Engineering Minerals co.	no-discribed	pH 7.0	6900cm ² /g	Ca 150ppm Na 200ppm KCl 2.3mol/l	20g +180g (sea sand)	22± 2 °C	no-discribed	no-discribed	26.4×10 ⁻⁴ mol/ℓ/h
					1250cm ² /g						7.0×10 ⁻⁴ mol/ℓ/h
					1050cm ² /g						7.9×10 ⁻⁴ mol/ℓ/h
A. F. Umana	1980	no-discribed	2.5N HCl washing (3 times)	pH 7.0	<200mesh	NaCl 0.01M	200mg/ℓ	25°C	no-discribed	350 ~650rpm	$d(FeS_2)/dt = K_p(FeS_2)$ $K_p = 1.6 \times 10^{-5}/s$
						NaCl 0.1 M					$K_p = 1.27 \times 10^{-5}/s$
						NaCl 1.0 M					$K_p = 0.7 \times 10^{-5}/s$
						NaCl 0.1M +Ni ²⁺ 10 ⁻⁴ M					$K_p = 2.2 \times 10^{-5}/s$
						NaCl 0.1M +Ni ²⁺ 10 ⁻⁵ M					$K_p = 1.9 \times 10^{-5}/s$
						NaCl 0.1M +Cu ²⁺ 10 ⁻⁴ M					$K_p = 2.5 \times 10^{-5}/s$
						NaCl 0.1M +Cu ²⁺ 10 ⁻⁵ M					$K_p = 1.6 \times 10^{-5}/s$
						Rico, Colorado					$K_p = 7.0 \times 10^{-5}/s$
						Custer, South Dakota					$K_p = 1.3 \times 10^{-5}/s$
						Appalachian coal Pennsylvania					$K_p = 6.4 \times 10^{-5}/s$
V. S. T. Ciminelli	1986	Huanzala, Peru	3N HCl washing +distilled water washing +acetone washing	HCl (pH1.5, 2.5) distilled water (pH5.5) Na ₂ CO ₃ (pH 10.5~12.5)	<400 mesh 400~270mesh 270~200mesh 200~150mesh 150~100mesh	1 mol/ℓ Na ₂ CO ₃	1 g/1 ℓ	50~84°C	no-discribed	no-discribed	$(1-X)^{-2/3} - 1 = K_{..t}$ $K_{..t} > 0.99/h$
N. Sakai	1987	Sakuhara mine Okayama, Japan	2N HCl washing	pH 0.3 pH 0.5 pH 1.2 pH 1.9	270~200mesh	distilled water	5 g/300ml	40, 50°C	no-discribed	300, 500, 800 rpm	$d[Fe^{2+}]/dt = \gamma_1 + \gamma_2$ $\gamma_1 = k_1[Fe^{3+}]^{0.8}[Fe^{2+}]^{-1.4}$ $\gamma_2 = k_2[H^+]^{-0.5}[Fe^{3+}]^{0.8}[Fe^{2+}]^{-1.4}$
H. K. Lin	1986	Keenecott's Bingham mine, Utah	no-discribed	no-discribed	270~200mesh	distilled water	5 g/500ml	90°C	no-discribed	no-discribed	$k = 2.2 \times 10^9 \exp(-9140/T)$ $8.21 \times 10^{-3} (cm^3/mol)^{1/2}/h$
								75°C			$2.54 \times 10^{-2} (cm^3/mol)^{1/2}/h$

1.3 緑泥石

緑泥石 (chlorite) は、蛇紋石, $Mg_{12}Si_8O_{20}(OH)_{16}$ とアメサイト, $(Mg_8Al_4)(Si_4Al_4)O_{20}(OH)_{16}$ の固溶体であり、理想化学式は $(Mg, Fe^{II}, Al)_{12}(Si, Al)_8O_{20}(OH)_{16}$ である。緑泥石の溶解速度の調査結果を表1.3.1 にまとめて示す。

1.3.1 溶解速度式

Ross⁴⁾ は、緑泥石の溶解速度が放物線的溶出速度式によることを示している。

$$\alpha^2 = k t \quad (1.3.1)$$

α : 溶解した量と初期に存在した量の比
k : 反応定数
t : 時間

また、溶解反応が拡散律速過程であり、円盤状の形状をした粒子試料の円周部が選択的に溶解反応している場合には、次式が適用可能であることが示されている。

$$\{1 - (1 - \alpha)^{1/2}\}^2 = K t \quad (1.3.2)$$

K : 反応定数

Table 1.3.1 Data base of leaching rate for chlorite

Author	Year	The place of origin	Pre-treatment	Solution pH	Surface area	Solution	Solid solution ratio	Temperature	Filtration	Shaking	Leaching rate
G. J. Ross	1967	Brewster, New York	no-discribed	no-discribed	<0.2 μm 5.7% 0.2~0.5 μm 19.0% 0.5~1.0 μm 29.5% 1.0~1.5 μm 33.8% 1.5~2.0 μm 12.0%	2.0N HCl	200mg/100ml	20, 30, 40 50, 60°C	Centri- fugation	no-discribed	no-discribed
N. G. Swoboda	1993	Eastern maine, USA Soil (Light-mineral fraction)	gravity- separation	pH 4.0	0.08m ² /g	HCl solution	5~10g/5ml/min.	no-discribed	no-discribed	no-shaking (Fluidized bed reactor)	6.7 $\mu\text{mol}/\text{m}^2/\text{s}$
				pH 4.5							3.8 $\mu\text{mol}/\text{m}^2/\text{s}$
		Soil (Heavy-mineral fraction)		pH 4.0							2.7 $\mu\text{mol}/\text{m}^2/\text{s}$
				pH 4.5							3.3 $\mu\text{mol}/\text{m}^2/\text{s}$
H. T. Voskresenskaya	1983	Cuba	no-discribed	pH 5.0	no-discribed	0.15M (NH ₄) ₂ HCO ₃	100mg/100ml	95±1°C	no-discribed	no-discribed	no-discribed
		GDR									no-discribed
Hayashi	1990	Wanibuchi mine, Shimane, Japan	washing + 105 °C drying	no-discribed	<0.2 μm (37.1m ² /g)	0.1M tiron solution (C ₆ H ₄ Na ₂ O ₈ S ₂)	25mg/30ml	80°C	Centri- fugation (5000rpm, 10 min.)	no-discribed	Leaching could not be observed

1.4 緑簾石

緑簾石 (epidote)は、 $X_2Y_3Z_3(O, OH, F)_{13}$ 、 $X = Ca, Cs^{III}, La^{III}, Y^{III}, Th, Fe^{II}, Mn^{II}, Mn^{III}, Y = Al, Fe^{III}, Mn^{III}, Fe^{II}, Mn^{II}, Ti, Z = Si, Be$ の組成を有する鉱物族の名称であり、ゾイサイト、クリノゾイサイト、紅簾石、その他の多くの鉱物に細分化される。また、細分化した鉱物の一つとしても緑簾石が定義されており、この場合の理想組成式は $Ca_2Fe^{III}Al_2O \cdot OH \cdot Si_2O_7 \cdot SiO_4$ である。

緑簾石の溶解速度に関しては、Rose⁵⁾の文献のみが検索された。その内容を表1.4.1に示した。

Table 1.4.1 Data base of leaching rate for epidote

Author	Year	The place of origin	Pre-treatment	Solution pH	Surface area	Solution	Solid solution ratio	Temperature	Filtration	Shaking	Leaching rate
N. M. Rose	1991	Dixie Vallery, Nevada	conc. HNO ₃ washing + ion-exchange water washing	pH 1.4~10.8	250~104 μm (0.169~0.368 m ² /g)	pH buffer solution	0.5 ~ 1 g / 100~150ml	25~90°C	no-discribed	250 ~500rpm	10 ⁻¹⁴ ~10 ⁻¹³ mol/cm ² /s
					104~ 53 μm (0.280~0.376 m ² /g)						10 ⁻¹⁴ ~10 ⁻¹³ mol/cm ² /s

1.5 菱鉄鉱

菱鉄鉱(siderite)の化学組成は FeCO_3 である。

菱鉄鉱の溶解速度に関しては、Greenberg ら⁶⁾の文献のみが検索された。Greenberg らは、合成した鉄炭酸塩の結晶を用いた溶解析出反応に関する試験から、溶解速度を評価している。その内容を表1.5.1 に示した。

Table 1.5.1 Data base of leaching rate for siderite

Author	Year	The place of origin	Pre-treatment	Solution pH	Surface area	Solution	Solid solution ratio	Temperature	Filtration	Shaking	Leaching rate
J. Greenberg	1992	synthesis ferrous carbonate	deoxygenated water washing	no-discribed	$1.5 \pm 0.1 \mu\text{m}$ ($1.05 \pm 0.09 \text{ m}^2/\text{g}$)	deoxygenated water (sparged with CO ₂ gas)	5.639g/750ml	26°C	no-discribed	mixing	first order empirical relation $\text{Ln}[(\text{Fe}_{\text{e,t}} - \text{Fe}_0)/(\text{Fe}_{\text{e,t}} - \text{Fe}_0)] = K_d(S/V)t$ $1.529 \times 10^{-4} \text{ l/m}^2/\text{s}$ second order empirical relation $1/(\text{Fe}_{\text{e,t}} - \text{Fe}_0) - 1/(\text{Fe}_{\text{e,t}} - \text{Fe}_0) = K_d(S/V)t$ $0.0534 \text{ l}^2/\text{mol/m}^2/\text{s}$
								60°C			first order empirical relation $2.651 \times 10^{-5} \text{ l/m}^2/\text{s}$ second order empirical relation $0.343 \text{ l}^2/\text{mol/m}^2/\text{s}$

Reference)

- 1) V. S. T. Ciminelli, K. Osseo-Asare, Kinetics of pyrite oxidation by oxygen in sodium carbonate solution, Hydrometall. React. Des. Kinet., Proc. Symp., pp.129-147, 1986.
- 2) K. Osseo-Asare, Pyrite in aqueous systems : semiconductor properties, oxidative dissolution and environmental control, Int. Conf. Process. Mater. Prop. (conference proceeding), pp.83-89, 1993.
- 3) H. K. Lin, H. Y. Sohn et al., The kinetics of leaching of chalcopyrite and pyrite grains in primary copper ore by dissolved oxygen, Hydrometall. React. Des. Kinet., Proc. Symp., pp.149-168, 1986.
- 4) G. J. Ross, Kinetics of acid dissolution of an orthochlorite mineral, Can. J. Chem., Vol.45, No.24, pp.3031-3034, 1967.
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- 6) J. Greenberg and M. Tomson, Precipitation and dissolution kinetics and equilibria of aqueous ferrous carbonate vs temperature, Applied Geochemistry, Vol.7, No.2, pp.185-190, 1992.

第2章 鉱物-水反応試験による反応速度データの取得

平成6年度は溶解速度データの整備が行われていない鉱物のうち、黄鉄鉱 (Pyrite, FeS_2) 及び緑泥石 (Chlorite, $(\text{Mg, Fe, Al})_{12}(\text{Si, Al})_8\text{O}_{20}(\text{OH})_{16}$) について溶解速度を測定した。

2.1 黄鉄鉱の溶解試験

2.1.1 試験方法

(1) 試験試料

(a) 黄鉄鉱

柳原鉱山 (岡山県久米郡) 産の黄鉄鉱を使用した。

試料の化学組成を表2.1.1 に示す。

Table 2.1.1 Elemental composition of pyrite sample

(wt-%)

Element	Pyrite
Fe	45.6
S	50.6
Cu	0.05
Na_2O	<0.01
K_2O	<0.01
MgO	0.12
CaO	0.05
Al_2O_3	0.04
SiO_2	2.09
Total	98.55

(b) 蒸留水

市販品の蒸留水 (和光純薬工業製) を使用した。

(2) 溶解試験

(a) 試料の調整

黄鉄鉱の粒径は32~20mesh (0.50~0.84mm) に調整した。試料は、アセトンで3回洗浄し、雰囲気制御グローブボックス内で1N 塩酸に浸漬した後、蒸留水で洗浄した。

(b) 溶解試験

還元雰囲気及び大気平衡の2種類の蒸留水について、黄鉄鉱の溶解試験を実施した。試験条件を表2.1.1、試験手順を図2.1.1 (1)~(2)に示す。

Table 2.1.2 Condition of leaching test for pyrite

Item	Condition
Atomosphere	Ar gas atomosphere
Test method	Batch method
Mineral	Pyrite
Particle size	20~32mesh (0.50~0.84mm)
Solution	①Reduced distilled water (NH ₂ NH ₂ 0.05mol/l) ②Distilled water (equilibrium with air)
Solid solution ratio	10.0g / 50ml
Leaching period	1, 2, 3, 7, 14, 28, 56, 84 days
Temparature	21±6 °C
Bottle	①Poly propylene bottle (100ml) ②Teflon bottle (60ml)
Filtration	0.2 μm membrane filter
Analysis method	{ solution : pH, Eh --- Electrode Fe, S --- ICP or ICP-mass solid : --- SEM, EDX

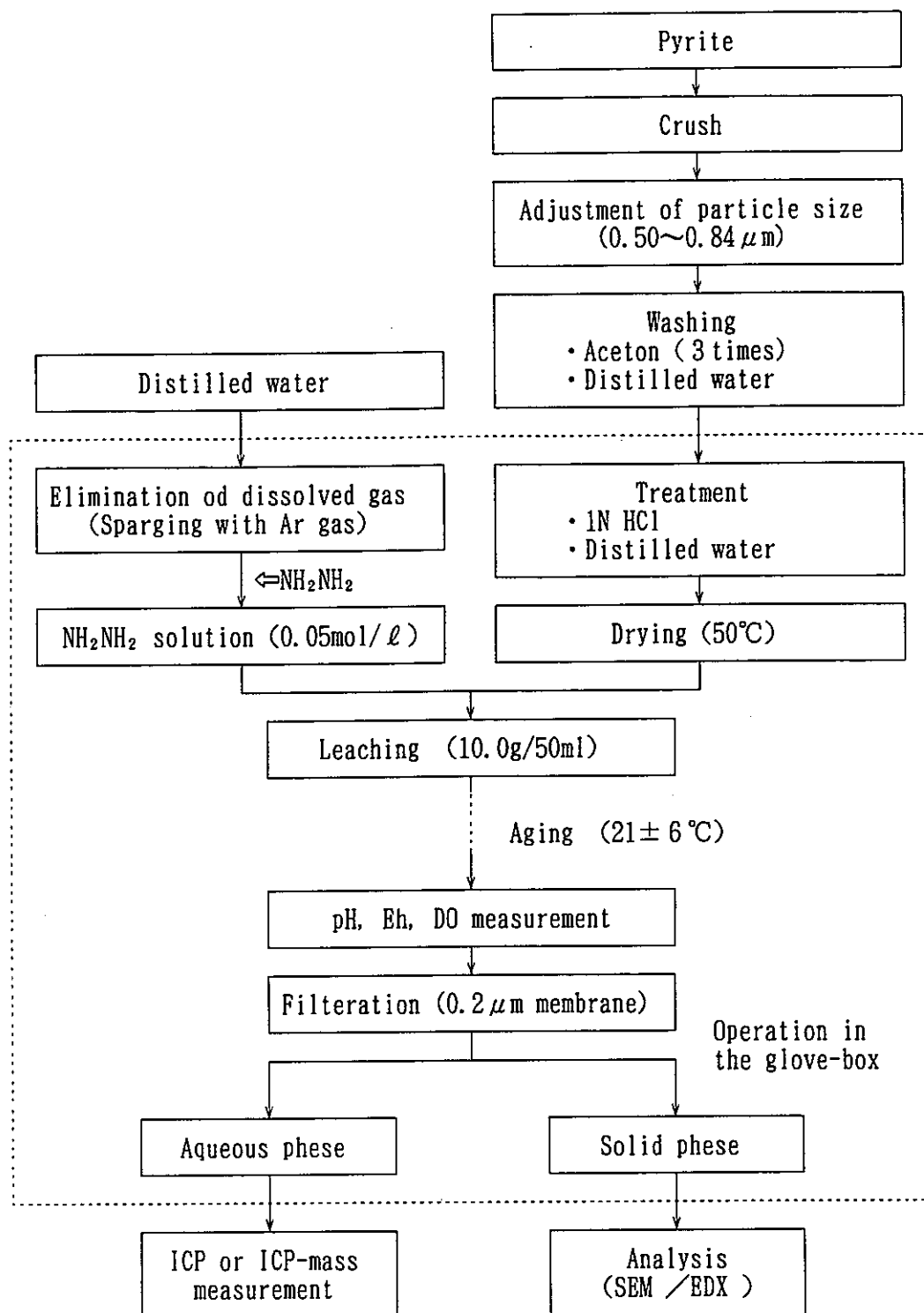


Figure 2.1.1 (1) Flow chart of leaching test for pyrite (reduced distilled water)

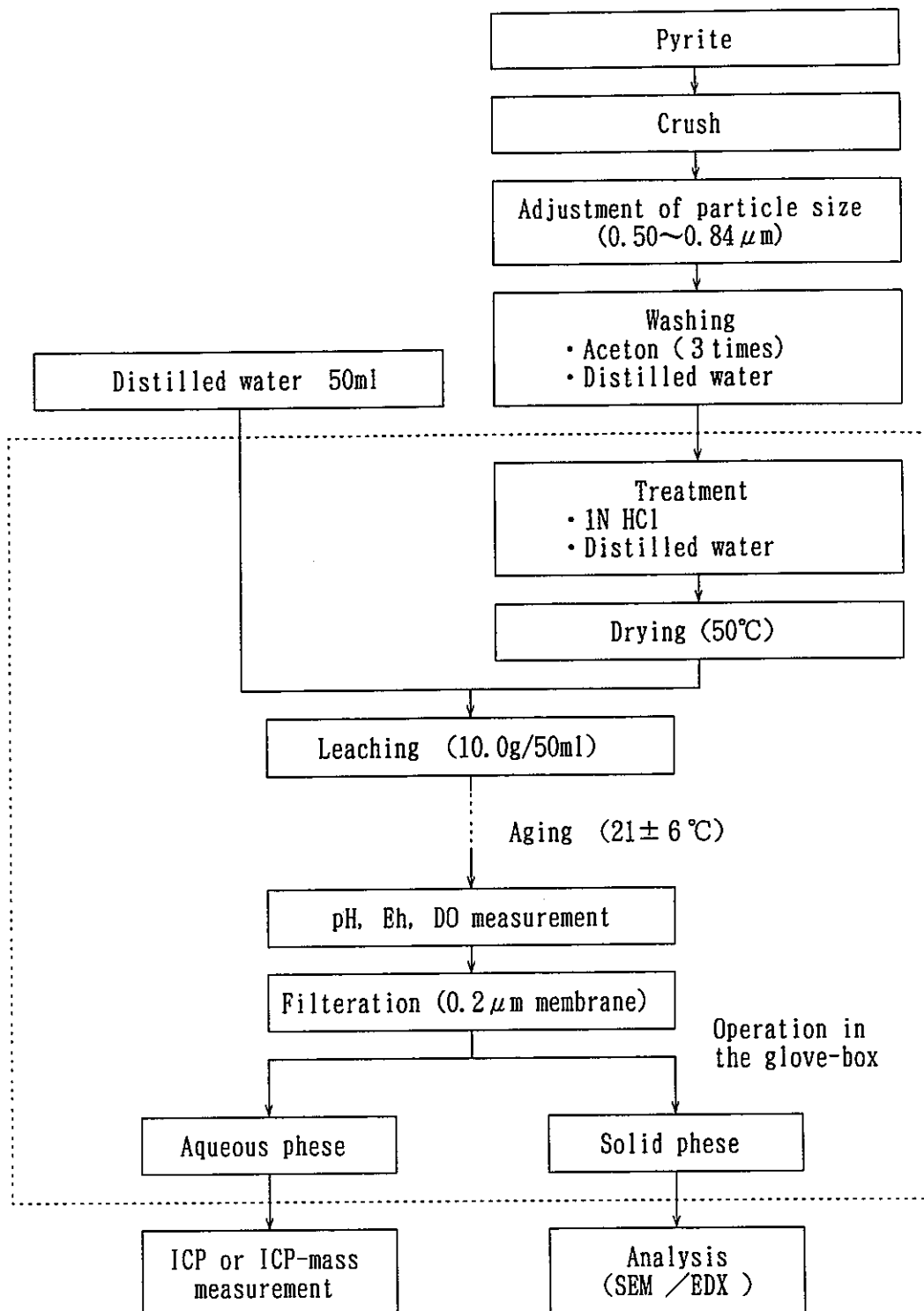


Figure 2.1.1 (2) Flow chart of leaching test for pyrite
(distilled water in equilibrium with air)

2.1.2 試験結果

(1) 溶解試験

溶解試験の結果を図2.1.2 (1)~(4)に示す。図2.1.2 (2)に示した pe は、以下の式により算出した。

$$pe = [F / (2.303 \cdot R \cdot K)] \cdot Eh \quad (2.1.1)$$

F : ファラデー定数 (96500 c/mol)

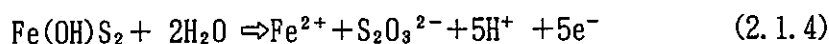
R : 気体定数 (8.31 J/mol/K)

K : 絶対温度

Eh : 酸化還元電位 (mV)

全体的な傾向として、還元雰囲気及び大気平衡の蒸留水とも、黄鉄鉱の溶解反応の進行とともに溶液中の還元雰囲気は高くなることが観察された。Feの総溶解量とSの溶解量との間に化学量論的な関係は認められなかった。

黄鉄鉱の溶解反応として、Osseo-Asare¹⁾ により以下の反応が示されている。



上記の溶解反応では、黄鉄鉱の溶解に従って e^- が放出され、酸化還元電位が低下(還元雰囲気にシフト)することが予想される。また、同時に H^+ も放出されることから、pHの低下も予想される。しかし、試験の結果では、酸化還元電位は低下するものの、pHについては逆に上昇する傾向であった。pHが低下しなかった原因として、溶液中に放出された H^+ は同時に放出される e^- により還元され、 H_2 ガスとなってしまったため、pHに影響しなくなったことが考えられる。実際に試験期間中にガスが発生し、試験容器が膨張することも観察されている。

還元雰囲気及び大気平衡の蒸留水とも弱アルカリ性であり、 e^- の放出量が H^+ よりも多いために酸化還元電位は低下し、それによってpHは上昇したものと考えられる。

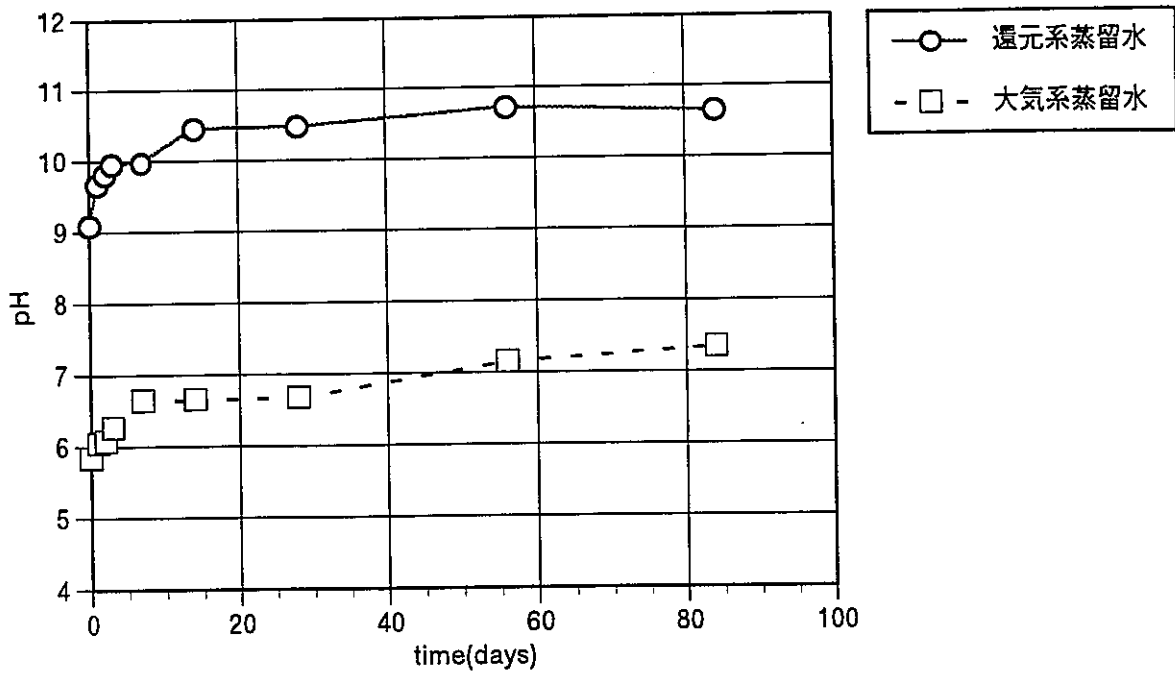


Figure 2.1.2(1) pH depend on leaching time for pyrite

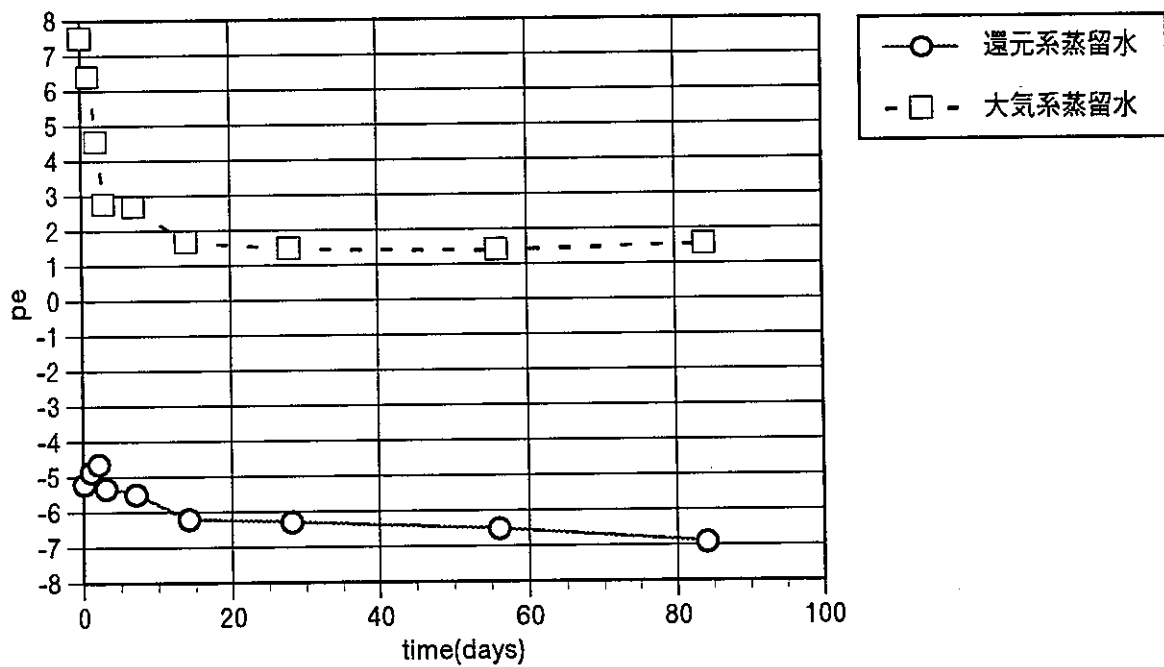


Figure 2.1.2(2) pe depend on leaching time for pyrite

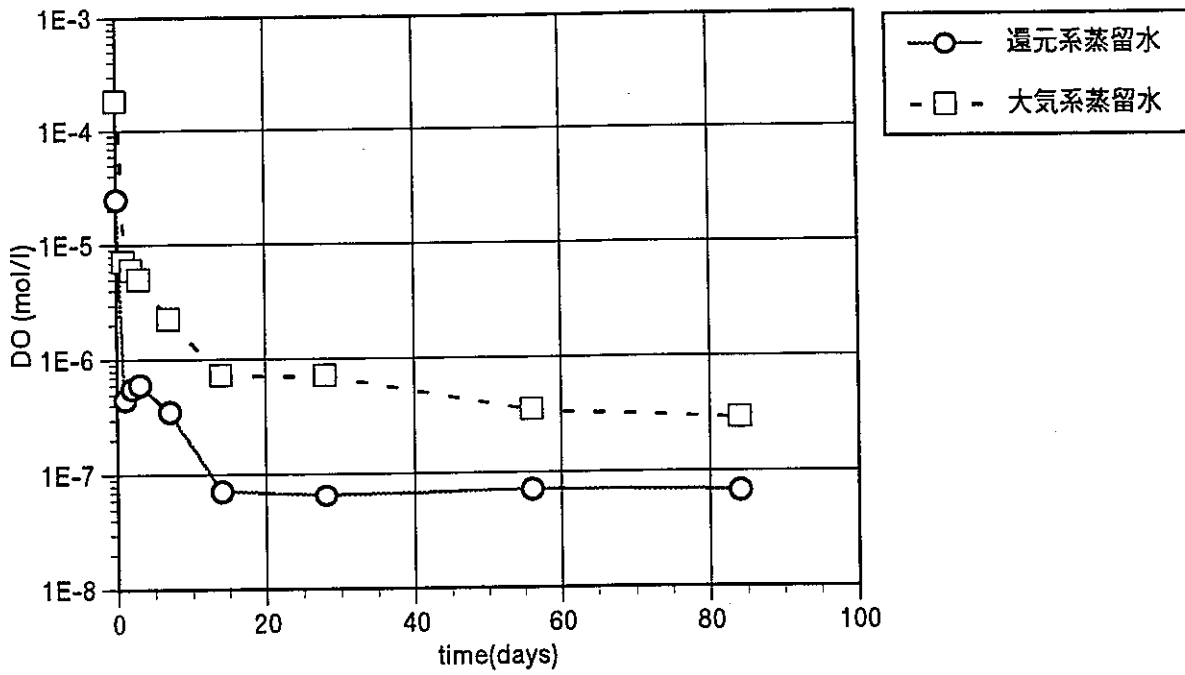


Figure 2.1.2(3) Do depend on leaching time for pyrite

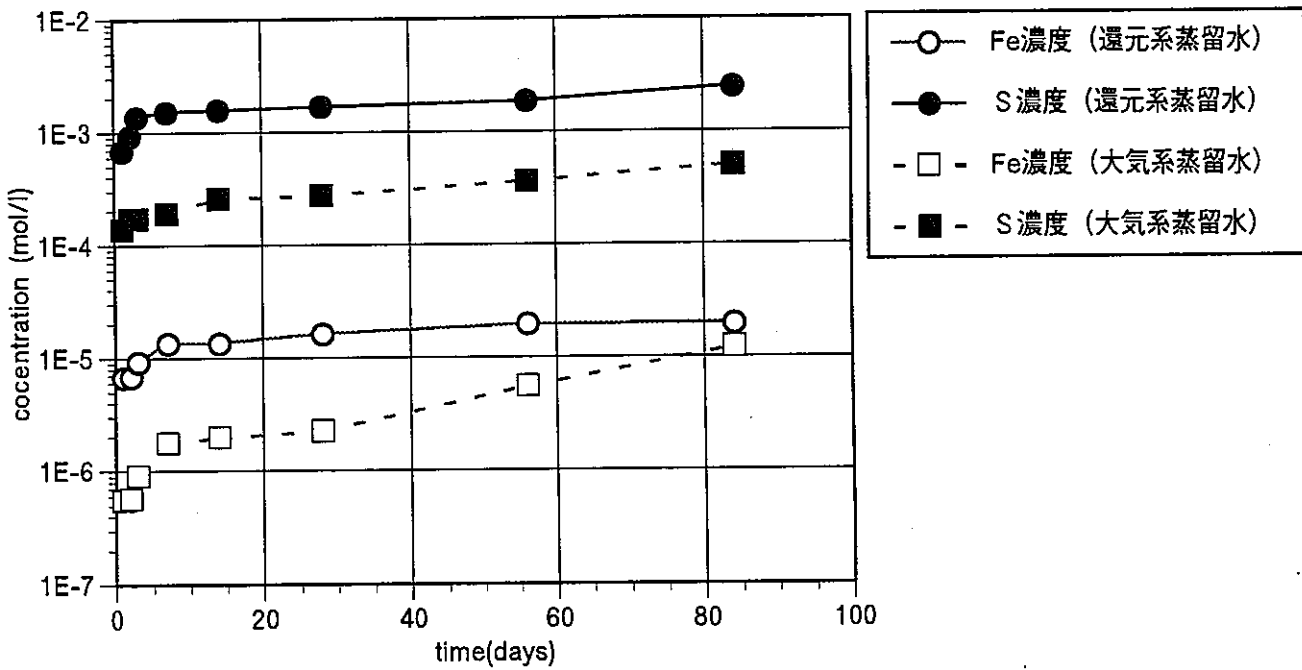


Figure 2.1.2(4) Fe and S depend on leaching time for pyrite

(2) 試料の表面分析

(a) SEM による写真観察

56日間の溶解試験終了後に黄鉄鉱試料の表面観察を行った結果、還元雰囲気及び大気平衡の蒸留水の場合とも、変質層等の異状は確認されなかった。

(b) EDX による元素測定

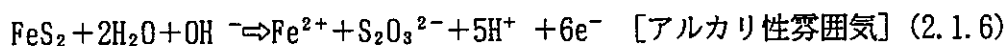
SEM の場合と同様、56日間の溶解試験終了後に黄鉄鉱試料の元素の濃度分布を深さ方向に沿って測定した結果、還元雰囲気及び大気平衡の蒸留水の場合とも、特定元素の溶脱等の変質は確認されなかった。

2.1.3 溶解速度の評価

(1) 還元雰囲気中の蒸留水

酸素濃度が低い還元雰囲気中での黄鉄鉱の溶解速度式は知られていない。よって、ここではOsseo-Asare¹⁾により示されている溶解反応式を仮定して、黄鉄鉱の溶解度積を求めることとした。

2.1.2で既述した溶解反応をまとめると以下の式となる。



溶解試験において測定されたpHが弱アルカリ領域であることから、ここでは溶解反応として、2.1.6式を仮定し、84日後の測定データから溶解度積(K)を求めることとした。溶解度積の算出式を2.1.7～2.1.8式に示す。

$$K = \frac{(\text{Fe}^{2+}) (\text{S}_2\text{O}_3^{2-}) (\text{H}^+)^5 (\text{e}^-)^6}{(\text{FeS}_2) (\text{H}_2\text{O})^2 (\text{OH}^-)} = \frac{(\text{Fe}^{2+}) (\text{S}_2\text{O}_3^{2-}) (\text{H}^+)^5 (\text{e}^-)^6}{(\text{OH}^-)} \quad (2.1.7)$$

$$\begin{aligned} \text{Log } K &= \text{Log}(\text{Fe}^{2+}) + \text{Log}(\text{S}_2\text{O}_3^{2-}) + 5\text{Log}(\text{H}^+) + 6\text{Log}(\text{e}^-) - \text{Log}(\text{OH}^-) \\ &= \text{Log}(\text{Fe}^{2+}) + \text{Log}(\text{S}_2\text{O}_3^{2-}) - 5\text{pH} - 6\text{pe} - (\text{pH} - 14) \\ &= \text{Log}(\text{Fe}^{2+}) + \text{Log}(\text{S}_2\text{O}_3^{2-}) - 6\text{pH} - 6\text{pe} + 14 \end{aligned} \quad (2.1.8)$$

但し、() は濃度 (mol/l)

その結果、還元雰囲気中での黄鉄鉱の溶解度積 (Log K) は-16.4と算定された。

(2) 大気平衡の蒸留水

酸素ガス存在下での溶解速度式として、Lin ら²⁾ は以下の式を示している。

$$1 - (1 - x)^{1/3} = k [O_2]^{1/2} t \quad (2.1.9)$$

x : 反応した黄鉄鉱のモル数
 [O₂] : 溶存酸素濃度
 t : 反応時間
 k : 反応速度定数

溶解試験の結果を $1 - (1 - X)^{1/3}$ と $[O_2]^{1/2} \cdot t$ の関係に整理し、図2.1.3 (1)~(2)に示した。黄鉄鉱の溶解についてはFe及びS の双方の濃度から評価した。

2.1.9 式を用いて反応速度定数kを求めた結果を表2.1.2 に示す。大気平衡の蒸留水中での溶解速度定数は、Fe濃度から評価した場合は $1.0 \times 10^{-4} \text{ (cm}^3/\text{mol)}^{1/2}/\text{h}$ 、S 濃度から評価した場合は $3.9 \times 10^{-3} \text{ (cm}^3/\text{mol)}^{1/2}/\text{h}$ であり、Lin ら²⁾ によって示されている文献値とオーダ的に一致した。

Table 2.1.3 Calculated reaction rate of pyrite by Lin's equation

Solution	Reaction rate k (cm ³ /mol) ^{1/2} /h		
	Measured data		Data by Lin et. ²⁾
Distilled water in equilibrium with air	Estimated by Fe	$(1.0 \pm 0.1) \times 10^{-4}$	8.21×10^{-3} (75°C) 2.54×10^{-2} (90°C)
	Estimated by S	$(3.9 \pm 0.5) \times 10^{-3}$	1.1×10^{-4} (25°C) *

注) ± : 標準偏差 1σ

* : Lin らによる温度依存式による推定値 [$k = 2.2 \times 10^9 \exp(-9140/T)$]

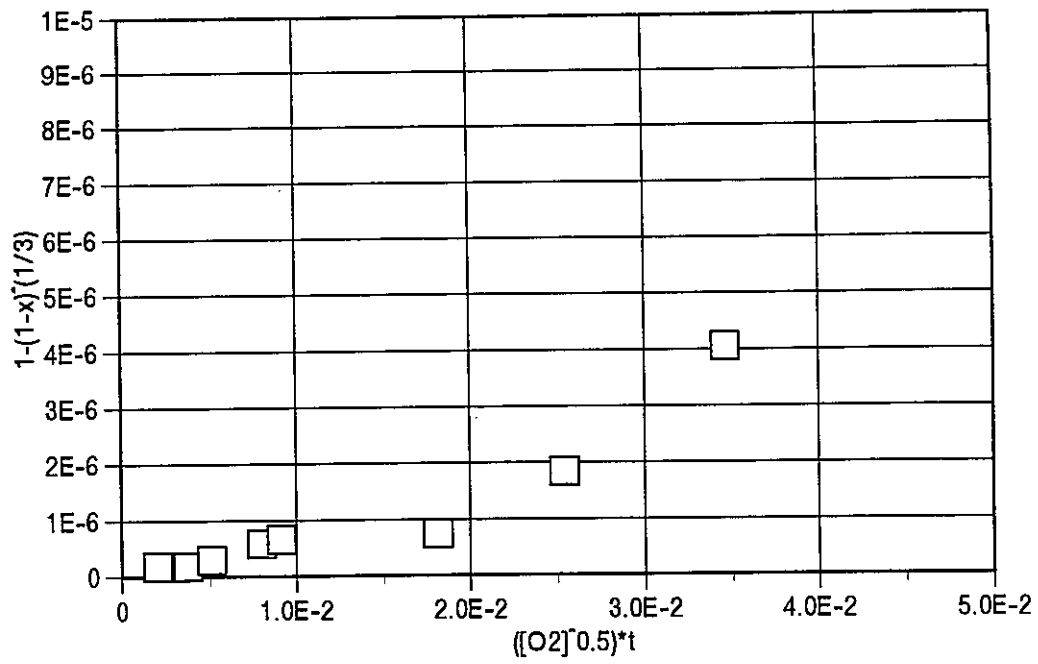


Figure 2.1.3(1) Relation of $[1-(1-x)^{1/3}]$ and $[(O_2)^{1/2}t]$ (Fe)

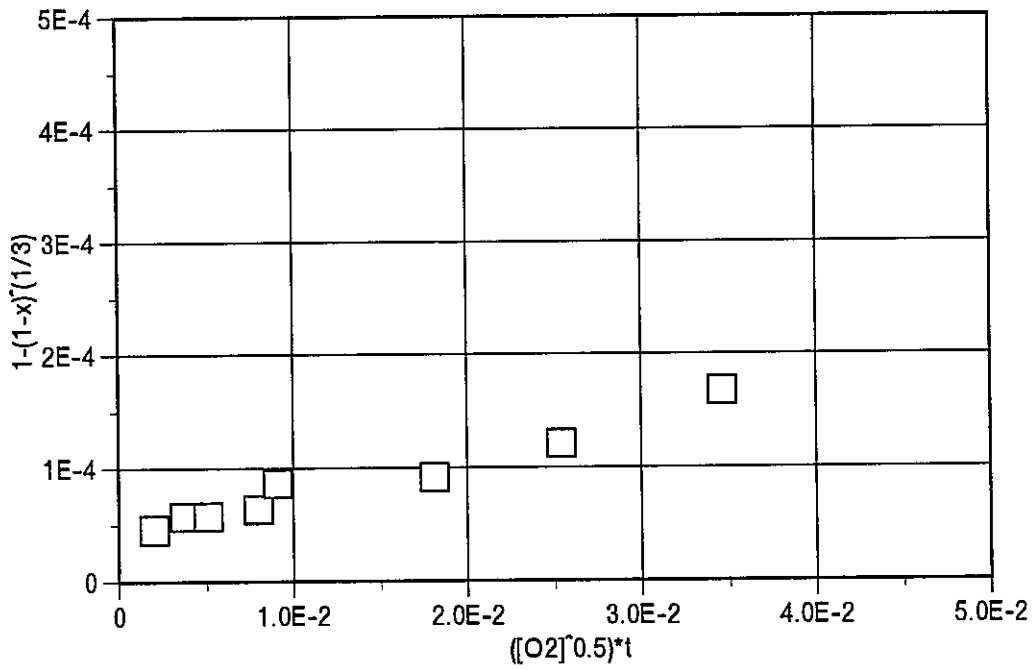


Figure 2.1.3(2) Relation of $[1-(1-x)^{1/3}]$ and $[(O_2)^{1/2}t]$ (S)

2.2 緑泥石の溶解試験

蒸留水及びpH 3 に調整した酸性蒸留水を対象に溶解速度を測定した。

2.2.1 試験方法

(1) 試験試料

(a) 緑泥石

高知県長岡郡本山町産の緑泥石を使用した。

緑泥石の化学組成を表2.2.1 に示す。

Table 2.2.1 Elemental composition of chlorite sample

(wt-%)

element	ratio
Na ₂ O	0.04
K ₂ O	0.04
MgO	32.90
CaO	0.43
Al ₂ O ₃	10.62
FeO	6.45
SiO ₂	31.40
合計	81.88

(b) 蒸留水

和光純薬工業(株)製の蒸留水を使用した。

(2) 溶解試験

(a) 試料の調整

緑泥石の粒径は32~20mesh (0.50~0.84mm) に調整した。試料は、アセトンで3回洗浄し、1N 塩酸に浸漬した後、pHが変化しなくなるまで蒸留水で洗浄した。

(b) 溶解試験

蒸留水及び塩酸によりpH 3 に調整した蒸留水を対象に、大気雰囲気中で溶解試験を行った。試験条件を表2.2.2、試験手順を図2.2.1 に示す。

Table 2.2.2 Condition of leaching test for chlorite

Item	Condition									
Test system	Air condition									
Test method	Batch method									
Sample	Chlorite									
Particle size	20~32mesh (0.50~0.84mm)									
Solution	①Distilled water ②pH3 distilled water									
Solid solution ratio	10.0g /50ml									
Test term	1, 3, 7, 10, 14, 28, 56, 84 days									
Temperature	25±1 °C									
Bottle	Poly-propylene bottle (100ml)									
Filtration	0.2 μm membrane filter									
Analysis method	<table style="border: none;"> <tr> <td style="border: none;">{</td> <td style="border: none;">solution : pH, Eh</td> <td style="border: none;">---- Electrode</td> </tr> <tr> <td style="border: none;"></td> <td style="border: none;">Mg, Fe Al, Si</td> <td style="border: none;">---- ICP or ICP-mass</td> </tr> <tr> <td style="border: none;">}</td> <td style="border: none;">solid :</td> <td style="border: none;">---- SEM, EDX</td> </tr> </table>	{	solution : pH, Eh	---- Electrode		Mg, Fe Al, Si	---- ICP or ICP-mass	}	solid :	---- SEM, EDX
{	solution : pH, Eh	---- Electrode								
	Mg, Fe Al, Si	---- ICP or ICP-mass								
}	solid :	---- SEM, EDX								

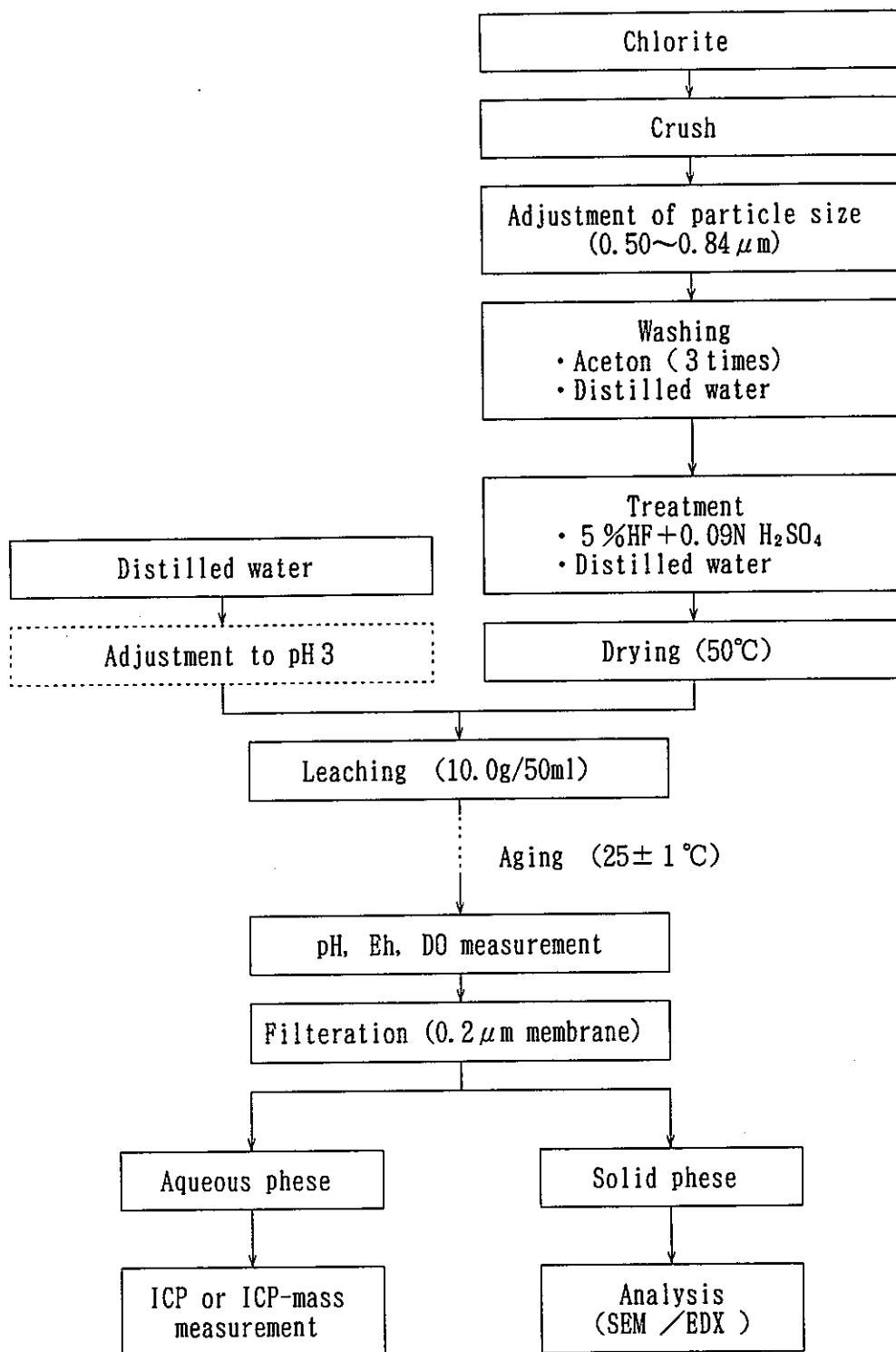


Figure 2.2.1 Flow chart of leaching test for chlorite

2.2.2 試験結果

(1) 溶解試験

蒸留水及びpH3の蒸留水（以下、酸性蒸留水）での緑泥石の溶解試験結果を図2.2.2 (1)~(3)に示す。Alについては試験期間中すべて定量下限以下（ $<3.7 \times 10^{-7} \text{ mol/l}$ ）であった。peは、以下の式により算出した。

$$pe = \left[F / (2.303 \cdot R \cdot K) \right] \cdot Eh \quad (2.2.1)$$

F : ファラデー定数 (96500 c/mol)
R : 気体定数 (8.31 J/mol/K)
K : 絶対温度
Eh : 酸化還元電位 (mV)

試験前の蒸留水のpHは5.85、酸性蒸留水は2.93であった。

蒸留水及び酸性蒸留水の場合とも、緑泥石の溶解により、pHは8.5程度に上昇した。pH及びEhの変化量は酸性蒸留水の方が大きかった。

Mg及びSi濃度については、酸性蒸留水の方が蒸留水よりも若干高い傾向にあるものの、その差は小さかった。

(2) 試料の表面分析

(a) SEM による写真観察

56日間の溶解試験終了後に緑泥石試料の表面観察を行った結果、変質層等の異状は確認されなかった。

(b) EDX による元素測定

SEM の場合と同様、56日間の溶解試験終了後に緑泥石試料のMg、Al及びSi元素の濃度分布を深さ方向に沿って測定した結果、特定元素の溶脱等の変質は確認されなかった。

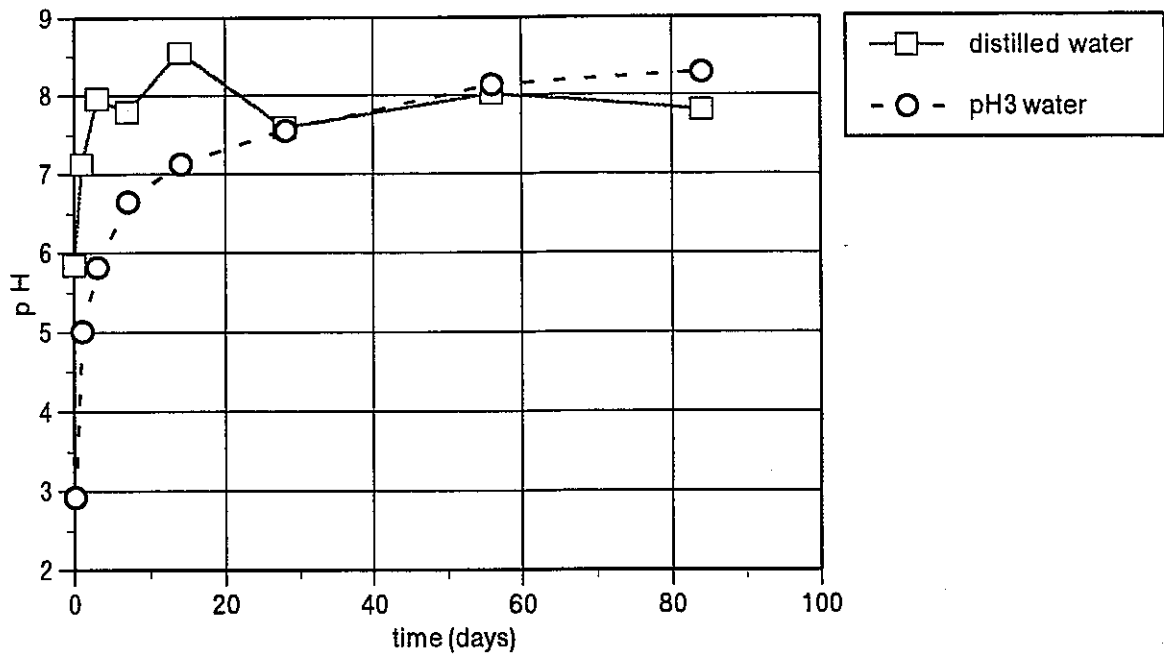


Figure 2.2.2(1) pH depend on leaching time for chlorite

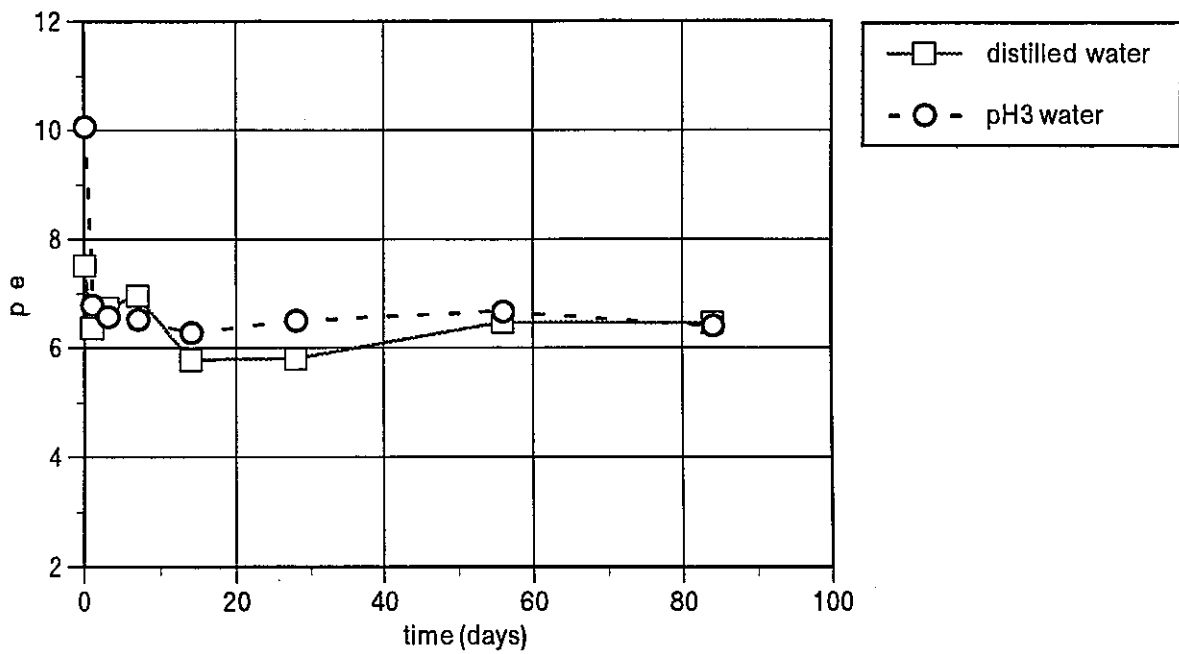


Figure 2.2.2(2) pe depend on leaching time for chlorite

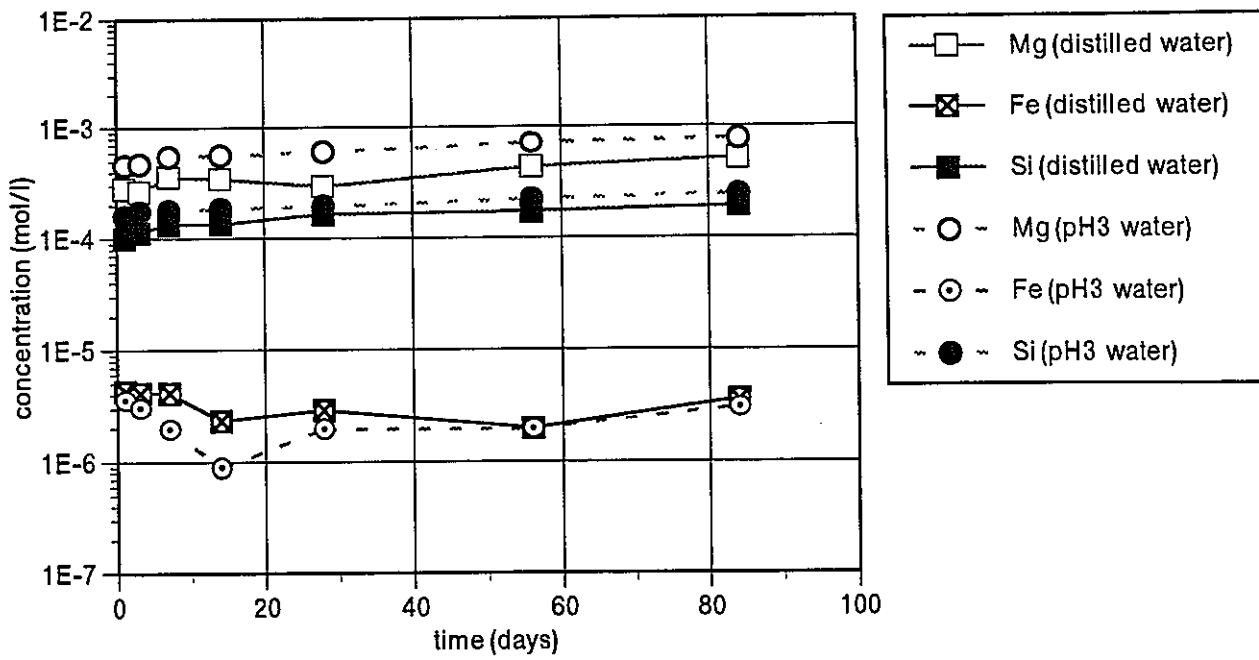


Figure 2.2.2(3) Mg,Fe,Si depend on leaching time for chlorite

2.2.3 溶解速度の評価

緑泥石の溶解反応について、Rossら³⁾は陽イオンの溶解量に化学量論的な関係があることを示しており、反応速度定数は溶解した量と初期に存在した量の比の二乗 (α^2) と時間 (t) の一次関係から評価できることを示している。Rossらによって示された溶解速度式を以下に示す。

$$\alpha^2 = k t \quad (2.2.2)$$

α : 溶解した量と初期に存在した量の比
 k : 反応定数
 t : 時間

溶解試験の結果から、2.2.2 式を用いて溶解速度定数 (K_1) を求めることにした。 α 値については、表2.2.1 に示した緑泥石の化学組成から算出した。

Mg及びSiの α^2 と時間 (t) の関係を図2.2.3 (1)~(2)に示す。最小自乗法により、 α^2 と t の傾きを求め、反応速度定数 (K_1) を算出した結果を表2.2.3 に示す。蒸留水及び酸性蒸留水とも、反応速度定数 (K_1) は $10^{-15} \sim 10^{-14}$ のオーダーであった。

Table 2.2.3 Estimated reaction rate(K_1) of chlorite by α^2

Solution	Estimated by Mg	Estimated by Si
Distilled water (pH 5.85)	$(9.3 \pm 1.7) \times 10^{-15}$	$(3.1 \pm 0.4) \times 10^{-15}$
Distilled water (pH 2.93)	$(2.1 \pm 0.2) \times 10^{-14}$	$(4.2 \pm 0.2) \times 10^{-15}$

注) \pm : 標準偏差 1σ

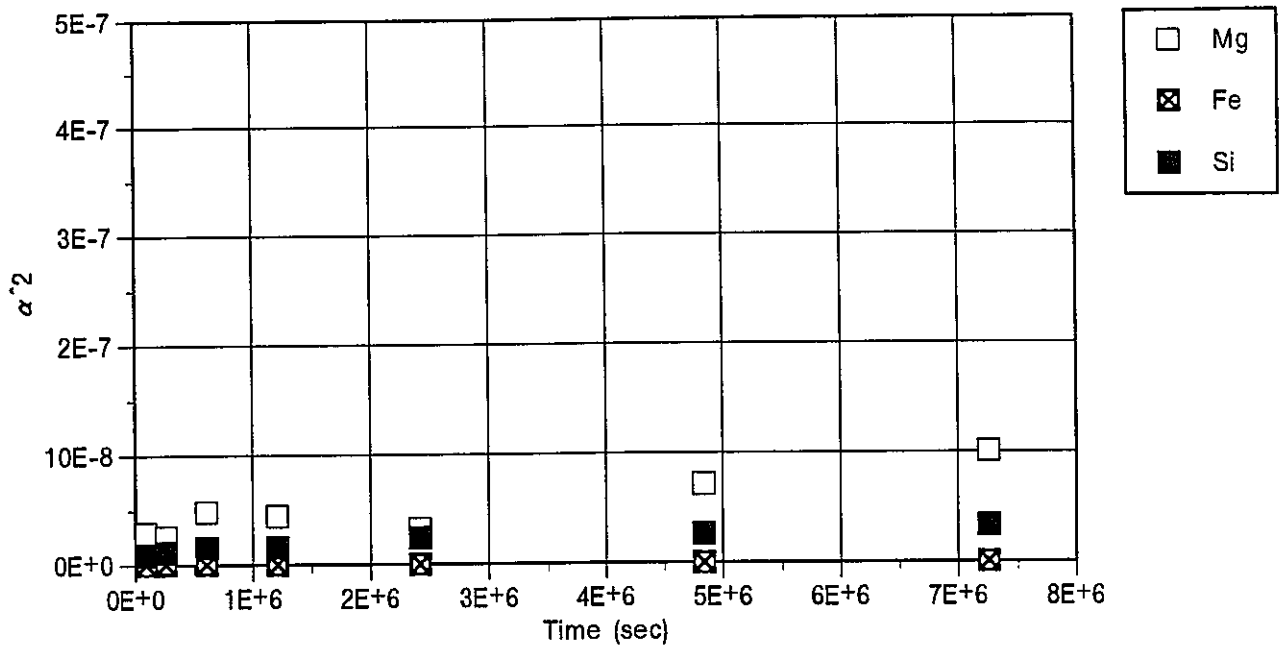


Figure 2.2.3(1) Relation of α^2 and leaching time (distilled water)

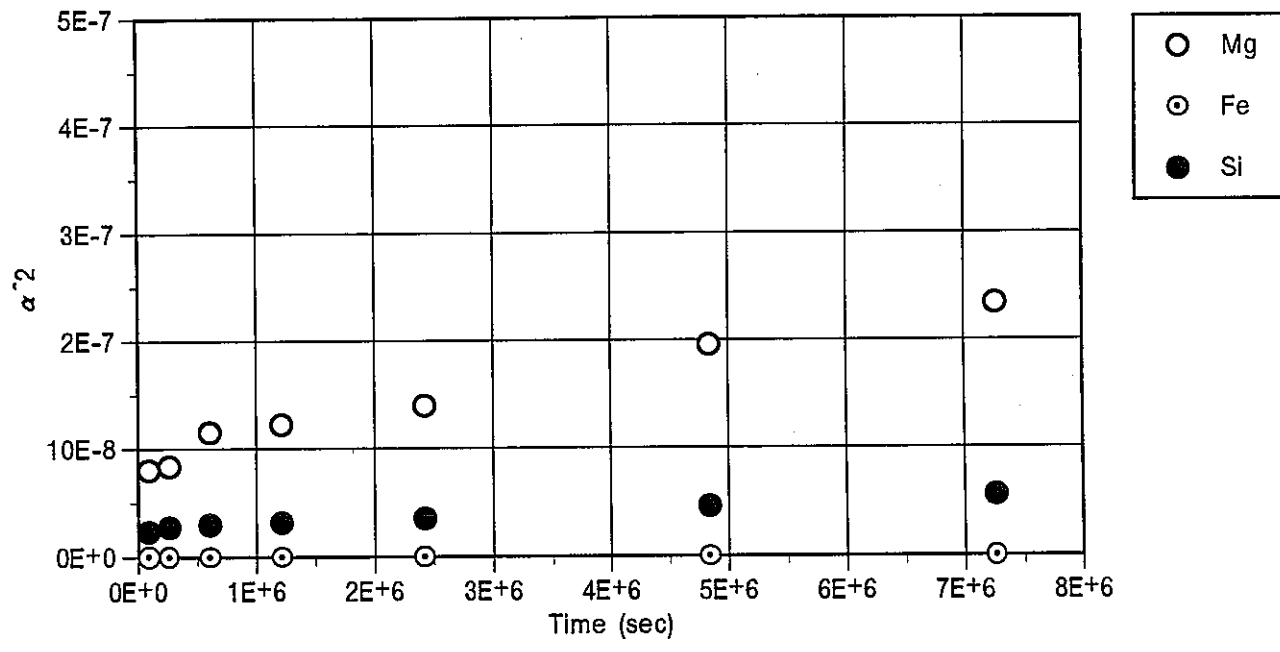


Figure 2.2.3(2) Relation of α^2 and leaching time (pH3 distilled water)

Reference)

- 1) K. Osseo-Asare. Pyrite in aqueous systems : semiconductor properties, oxidative dissolution, and environmental control, Int. Conf. Process. Mater. Prop. (conference proceeding), pp.83-89, 1993.
- 2) H. K. Lin, H. Y. Sohn, et al., The kinetics of leaching of chalcopyrite and pyrite grains in primary copper ore by dissolved oxygen, Hydrometall. React. Des. Kinet., Proc. Symp., pp.149-168, 1986.
- 3) G. J. Ross, Kinetics of acid dissolution of an orthochlorite mineral, Can. J. Chem., Vol.45, No.24, pp.3031-3034, 1967.

Investigation of Leaching Rate on Minerals
for Development of Groundwater Quality
Evolution Model

(Abstract)

Investigation of Leaching Rate on Minerals for Development of
Groundwater Quality Evolution Model

Hiroshi Tanaka*

Abstract

1. Survey on leaching rate of pyrite, chlorite, epidote and siderite.

(1) Pyrite

Reaction rate (K) is depended on dissolve O₂ concentration in Lin's literature.

$$1 - (1 - x)^{1/3} = k [O_2]^{1/2} \cdot t$$

(x : Mole number of dissolved FeS₂, [O₂] : Dissolve O₂ concentration.
t : Time)

Reaction rate is changed by temperature.

$$k = 2.2 \times 10^9 \exp(-9140/T)$$

(2) Chlorite

Reaction rate is measured $2.7 \sim 6.7 \times 10^{-12}$ mol/m²/s (pH3 ~4.5) by Swoboda-Colberg et al. Reaction rate is controlled by inner diffusion.

(3) Epidote

Reaction rate is measured $10^{-14} \sim 10^{-13}$ mol/cm²/s in pH 1~11 by Rose.

(4) Siderite

Reaction rate is measured 9.93×10^{-6} mol/m²/s in O₂-free solution by Greenberg et al.

2. Experimental study on leaching rate of minerals.

(1) Measurement of leaching rate of pyrite

Leaching rate of pyrite was measured in distilled water under redox condition. Reaction rate (K) was estimated $10^{-4} \sim 10^{-3}$ (cm³ · mol⁻¹)^{1/2} · h⁻¹ by Lin's rate equation. At 56 days in the experiments, altered layer could not be found in SEM and EDX observation.

(2) Measurement of leaching rate of chlorite

Leaching rate of chlorite was measured in distilled water under air condition. Disolution process of chlorite was parabolic stage, and reaction rate (K) was estimated order of $10^{-15} \sim 10^{-14}$ by Ross's rate equation.

$$\alpha^2 = k t$$

(α : dissolved mineral amount / initial mineral amount, t : time (sec))

At 56 days in the experiments, altered layer could not be found in SEM and EDX observation.

Work performed by Mitsubishi Materials Corporation under with Power Reactor and Nuclear Fuel Development Corporation.

Contract No. 060D0312

PNC Lieson : Yasuo Sasaki, Geological Isolation Development Section
Tokai Works.

*Naka Energy Reserch Center.

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1. Survey on leaching rate of pyrite, chlorite, epidote and siderite

1.1 Outline of survey

1.1.1 Minerals

The minerals of references researched were follows.

- ①Pyrite
- ②Chlorite
- ③Epidote
- ④Siderite

1.1.2 Data base

DIALOG data base was used in survey on leaching rate. Key words as follow were used.

(Mineral name) × (DISSOLUTION+LEACHING) × (RATE+KINETIC)

The number of references researched are shown in table 1.1.1.

Table 1.1.1 The number of references researched in DIALOG database

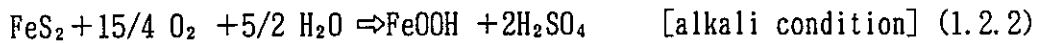
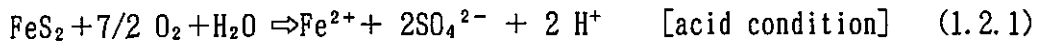
database	minerals			
	pyrite	chlorite	epidote	siderite
CA SEARCH	149	14	1	2
GEOREF	5	4	1	4

1.2 Pyrite

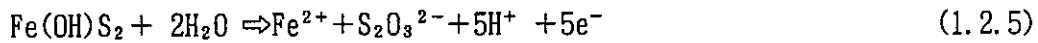
The summary of references researched is shown in table 1.2.1.

1.2.1 Leaching reaction

Ciminelli et al.¹⁾ indicated leaching reaction of pyrite as follows.



Also Osseo-Asare²⁾ indicated leaching reaction as follows.



1.2.2 Equation of leaching rate

Lin et al.³⁾ indicated equation of leaching rate in the presence of oxygen as follows. Leaching rate (K) is decided by relation of $1 - (1-X)^{1/3}$ and $[\text{O}_2]^{1/2} t$.

$$1 - (1-X)^{1/3} = k [\text{O}_2]^{1/2} t \quad (1.2.7)$$

X : mol amount of dissolve FeS_2
[O_2] : dissolve O_2 concentration
t : leaching time
k : leaching rate

Table 1.2.1 Data base of leaching rate for pyrite

Author	Year	The place of origin	Pre-treatment	Solution pH	Surface area	Solution	Solid solution ratio	Temperature	Filtration	Shaking	Leaching rate
T. Nagai	1968	Sasatani mine, Uku mine, Wagasennin mine, Washiai mine	no-discribed	no-discribed	no-discribed	1N H ₂ SO ₄	25cm ² /450ml	115 ~175 °C	no-discribed	0 ~800 rpm	0.1 ~10mg-Fe/cm ² /h
R. S. Schechter	1984	Combustion Engineering Minerals co.	no-discribed	pH 7.0	6900cm ² /g	Ca 150ppm Na 200ppm KCl 2.3mol/l	20g +180g (sea sand)	22± 2 °C	no-discribed	no-discribed	26.4 × 10 ⁻⁴ mol / l / h
					1250cm ² /g						7.0 × 10 ⁻⁴ mol / l / h
					1050cm ² /g						7.9 × 10 ⁻⁴ mol / l / h
A. F. Umana	1980	no-discribed	2.5N HCl washing (3 times)	pH 7.0	<200mesh	NaCl 0.01M	200mg/ l	25°C	no-discribed	350 ~650rpm	$d(FeS_2)/dt = K_p(FeS_2)$ $K_p = 1.6 \times 10^{-5}/s$
						NaCl 0.1 M					$K_p = 1.27 \times 10^{-5}/s$
						NaCl 1.0 M					$K_p = 0.7 \times 10^{-5}/s$
						NaCl 0.1M + Ni ²⁺ 10 ⁻⁴ M					$K_p = 2.2 \times 10^{-5}/s$
						NaCl 0.1M + Ni ²⁺ 10 ⁻⁵ M					$K_p = 1.9 \times 10^{-5}/s$
						NaCl 0.1M + Cu ²⁺ 10 ⁻⁴ M					$K_p = 2.5 \times 10^{-5}/s$
						NaCl 0.1M + Cu ²⁺ 10 ⁻⁵ M					$K_p = 1.6 \times 10^{-5}/s$
		Rico, Colorado	NaCl 0.1 M	$K_p = 7.0 \times 10^{-6}/s$							
		Custer, South Dakota	NaCl 0.1 M	$K_p = 1.3 \times 10^{-5}/s$							
		Appalachian coal Pennsylvania	NaCl 0.1 M	$K_p = 6.4 \times 10^{-6}/s$							
V. S. T. Ciminelli	1986	Huanzala, Peru	3N HCl washing +distilled water washing +acetone washing	HCl (pH1.5, 2.5) distilled water (pH5.5) Na ₂ CO ₃ (pH 10.5~12.5)	<400 mesh 400~270mesh 270~200mesh 200~150mesh 150~100mesh	1 mol/l Na ₂ CO ₃	1g/l l	50~84°C	no-discribed	no-discribed	$(1-X)^{-2/3} - 1 = K_{..} t$ $K_{..} > 0.99/h$
N. Sakai	1987	Sakuhara mine Okayama, Japan	2N HCl washing	pH 0.3 pH 0.5 pH 1.2 pH 1.9	270~200mesh	distilled water	5g/300ml	40, 50°C	no-discribed	300, 500, 800 rpm	$d[Fe^{2+}]/dt = \gamma_1 + \gamma_2$ $\gamma_1 = k_1 [Fe^{3+}]^{0.6} [Fe^{2+}]^{-1.4}$ $\gamma_2 = k_2 [H^+]^{-0.5} [Fe^{3+}]^n [Fe^{2+}]^{-1.1}$
H. K. Lin	1986	Keenecott's Bingham mine, Utah	no-discribed	no-discribed	270~200mesh	distilled water	5g/500ml	90°C	no-discribed	no-discribed	$k = 2.2 \times 10^9 \exp(-9140/T)$ $8.21 \times 10^{-1} (cm^3/mol)^{1/2}/h$
								75°C			$2.54 \times 10^{-2} (cm^3/mol)^{1/2}/h$

1.3 Chlorite

Chlorite is solid-solution mineral, and the ideal chemical composition is $(\text{Mg, Fe II, Al})_{12}(\text{Si, Al})_8\text{O}_{20}(\text{OH})_{16}$.

The summary of references researched is shown in table 1.3.1.

1.3.1 Equation of leaching rate

Ross⁴⁾ indicated leaching reaction of chlorite as follows.

$$\alpha^2 = k t \quad (1.3.1)$$

α : ratio of dissolve amount and initial amount
 k : leaching rate
 t : leaching time

Table 1.3.1 Data base of leaching rate for chlorite

Author	Year	The place of origin	Pre-treatment	Solution pH	Surface area	Solution	Solid solution ratio	Temperature	Filtration	Shaking	Leaching rate
G. J. Ross	1967	Brewster, New York	no-discribed	no-discribed	<0.2 μm 5.7% 0.2~0.5 μm 19.0% 0.5~1.0 μm 29.5% 1.0~1.5 μm 33.8% 1.5~2.0 μm 12.0%	2.0N HCl	200mg/100ml	20, 30, 40 50, 60°C	Centri- fugation	no-discribed	no-discribed
N. G. Swoboda	1993	Eastern maine, USA Soil (Light-mineral fraction)	gravity- separation	pH 4.0	0.08m ² /g	HCl solution	5 ~10g/5ml/min.	no-discribed	no-discribed	no-shaking (Fluidized bed reactor)	6.7 $\mu\text{mol}/\text{m}^2/\text{s}$
				pH 4.5							3.8 $\mu\text{mol}/\text{m}^2/\text{s}$
		Soil (Heavy-mineral fraction)		pH 4.0							2.7 $\mu\text{mol}/\text{m}^2/\text{s}$
				pH 4.5							3.3 $\mu\text{mol}/\text{m}^2/\text{s}$
H. T. Voskresens kaya	1983	Cuba	no-discribed	pH 5.0	no-discribed	0.15M (NH ₄) ₂ HClit	100mg/100ml	95 ± 1 °C	no-discribed	no-discribed	no-discribed
		GDR									no-discribed
Hayashi	1990	Wanibuchi mine, Shimane, Japan	washing + 105 °C drying	no-discribed	<0.2 μm (37.1m ² /g)	0.1M tiron solution (C ₈ H ₄ Na ₂ O ₈ S ₂)	25mg/30ml	80°C	Centri- fugation (5000rpm, 10 min.)	no-discribed	Leaching could not be observed

1.4 Epidote

The ideal chemical composition is $\text{Ca}_2\text{Fe IIIAl}_2\text{O} \cdot \text{OH} \cdot \text{Si}_2\text{O}_7 \cdot \text{SiO}_4$.

Rose's literature⁵⁾ was found in leaching rate of epidote.

The summary of references researched is shown in table 1.4.1.

Table 1.4.1 Data base of leaching rate for epidote

Author	Year	The place of origin	Pre-treatment	Solution pH	Surface area	Solution	Solid solution ratio	Temperature	Filtration	Shaking	Leaching rate
N. M. Rose	1991	Dixie Valley, Nevada	conc. HNO ₃ washing + ion-exchange water washing	pH 1.4~10.8	250~104 μm (0.169~0.368 m ² /g)	pH buffer solution	0.5 ~ 1 g / 100~150ml	25~90°C	no-discribed	250 ~500rpm	10 ⁻¹⁴ ~10 ⁻¹³ mol/cm ² /s
					104~ 53 μm (0.280~0.376 m ² /g)						10 ⁻¹⁴ ~10 ⁻¹³ mol/cm ² /s

1.5 Siderite

Chemical composition of siderite is FeCO_3 .

The literature by Greenberg et al.⁶⁾ was found leaching rate.

Greenberg et al. estimated leaching rate in experimentation by synthetic siderite.

The summary of references researched is shown in table 1.5.1.

Table 1.5.1 Data base of leaching rate for siderite

Author	Year	The place of origin	Pre-treatment	Solution pH	Surface area	Solution	Solid solution ratio	Temperature	Filtration	Shaking	Leaching rate
J. Greenberg	1992	synthesis ferrous carbonate	deoxygenated water washing	no-discribed	$1.5 \pm 0.1 \mu\text{m}$ ($1.05 \pm 0.09 \text{ m}^2/\text{g}$)	deoxygenated water (sparged with CO ₂ gas)	5.639g/750ml	26°C	no-discribed	mixing	first order empirical relation $\text{Ln}[(\text{Fe}_{\text{e},\text{t}} - \text{Fe}_0)/(\text{Fe}_{\text{e},\text{t}} - \text{Fe}_0)] = \text{Kd}(\text{S}/\text{V})t$ $1.529 \times 10^{-4} \text{ l}/\text{m}^2/\text{s}$ second order empirical relation $1/(\text{Fe}_{\text{e},\text{t}} - \text{Fe}_0) - 1/(\text{Fe}_{\text{e},\text{t}} - \text{Fe}_0) = \text{Kd}(\text{S}/\text{V})t$ $0.0534 \text{ l}^2/\text{mol}/\text{m}^2/\text{s}$
								60°C			first order empirical relation $2.651 \times 10^{-5} \text{ l}/\text{m}^2/\text{s}$ second order empirical relation $0.343 \text{ l}^2/\text{mol}/\text{m}^2/\text{s}$

Reference)

- 1) V.S.T. Ciminelli, K. Osseo-Asare, Kinetics of pyrite oxidation by oxygen in sodium carbonate solution, Hydrometall. React. Des. Kinet., Proc. Symp., pp.129-147, 1986.
- 2) K. Osseo-Asare, Pyrite in aqueous systems : semiconductor properties, oxidative dissolution and environmental control, Int. Conf. Process. Mater. Prop. (conference proceeding), pp.83-89, 1993.
- 3) H.K. Lin, H.Y. Sohn et al., The kinetics of leaching of chalcopyrite and pyrite grains in primary copper ore by dissolved oxygen, Hydrometall. React. Des. Kinet., Proc. Symp., pp.149-168, 1986.
- 4) G. J. Ross, Kinetics of acid dissolution of an orthochlorite mineral, Can. J. Chem., Vol.45, No.24, pp.3031-3034, 1967.
- 5) N.M. Rose, Dissolution rates of prehnite, epidote, and albite, Geochim. Cosmochim. Acta, Vol.55, No.11, pp.3273-3286, 1991.
- 6) J. Greenberg and M. Tomson, Precipitation and dissolution kinetics and equilibria of aqueous ferrous carbonate vs temperature, Applied Geochemistry, Vol.7, No.2, pp.185-190, 1992.

2. Experimental study on leaching rate of minerals

2.1 Measurement of leaching rate of pyrite

2.1.1 Experimental method

(1) Sample

(a) Pyrite

Pyrite sample was obtained from Yanahara mine (Okayama, Japan).

Elemental composition of sample was shown in table 2.1.1.

Table 2.1.1 Elemental composition of pyrite sample

(wt-%)

Element	Pyrite
Fe	45.6
S	50.6
Cu	0.05
Na ₂ O	<0.01
K ₂ O	<0.01
MgO	0.12
CaO	0.05
Al ₂ O ₃	0.04
SiO ₂	2.09
Total	98.55

(b) Distilled water

Distilled water was bought from Waco chemicals co.

(2) Leaching test

(a) Preparation of pyrite

Particle size was adjusted to 32~20mesh (0.50~0.84mm). The sample was washed 3 times by acetone, leached in 1N HCl solution, and washed by distilled water.

(b) Leaching test

Two kind of solution samples were prepared. One was reduced distilled water, another was distilled water in equilibrium with air.

Condition of leaching test was shown in table 2.1.2 and figure 2.1.1(1)~(2).

Table 2.1.2 Condition of leaching test for pyrite

Item	Condition
Atomosphere	Ar gas atomosphere
Test method	Batch method
Mineral	Pyrite
Particle size	20~32mesh (0.50~0.84mm)
Solution	①Reduced distilled water (NH_2NH_2 0.05mol/l) ②Distilled water (equilibrium with air)
Solid solution ratio	10.0g / 50ml
Leaching period	1, 2, 3, 7, 14, 28, 56, 84 days
Temparature	21 ± 6 °C
Bottle	①Poly propylene bottle (100ml) ②Teflon bottle (60ml)
Filtration	0.2 μm membrane filter
Analysis method	{ solution : pH, Eh Electrode Fe, S ICP or ICP-mass solid : SEM, EDX

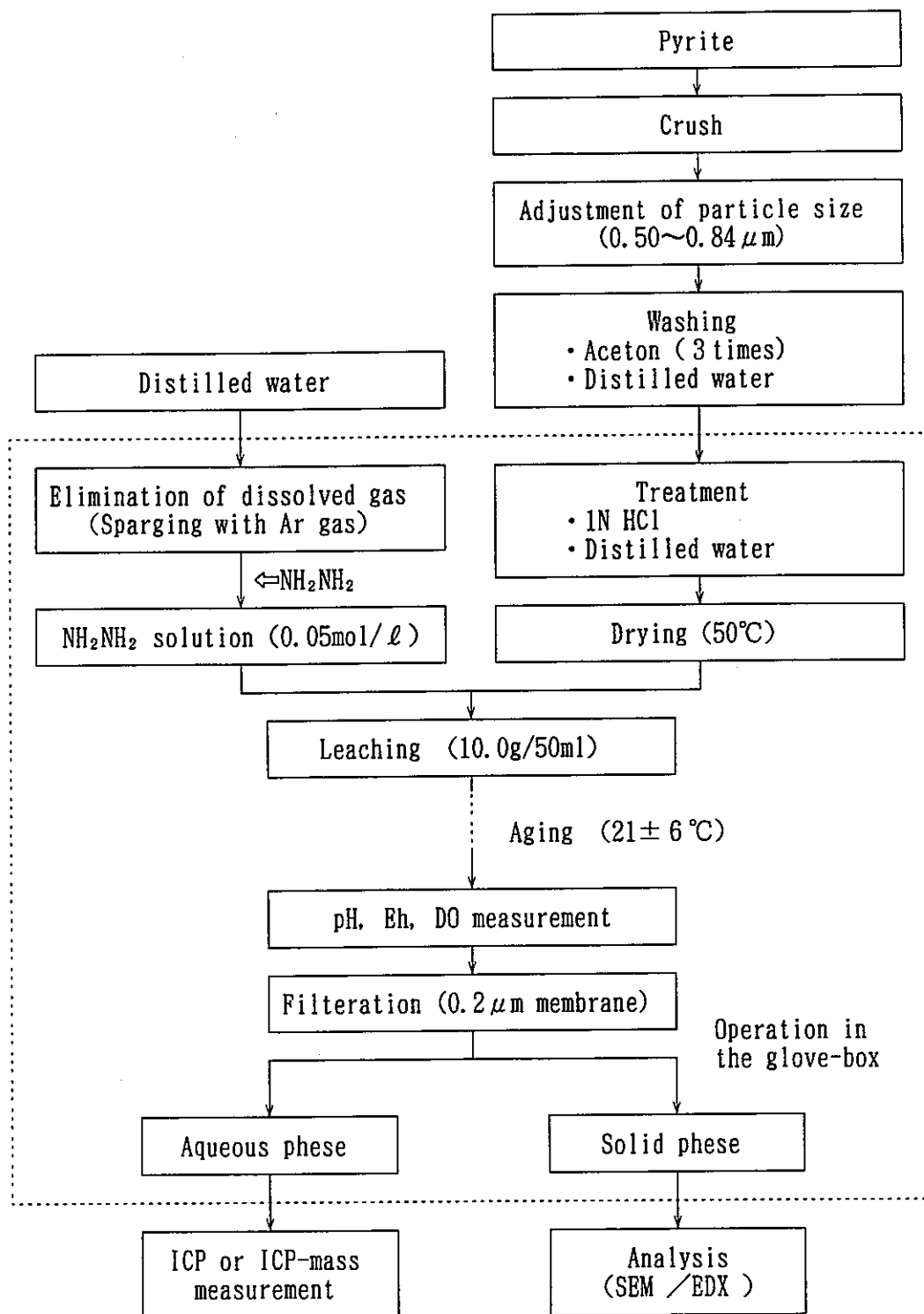


Figure 2.1.1 (1) Flow chart of leaching test for pyrite (reduced distilled water)

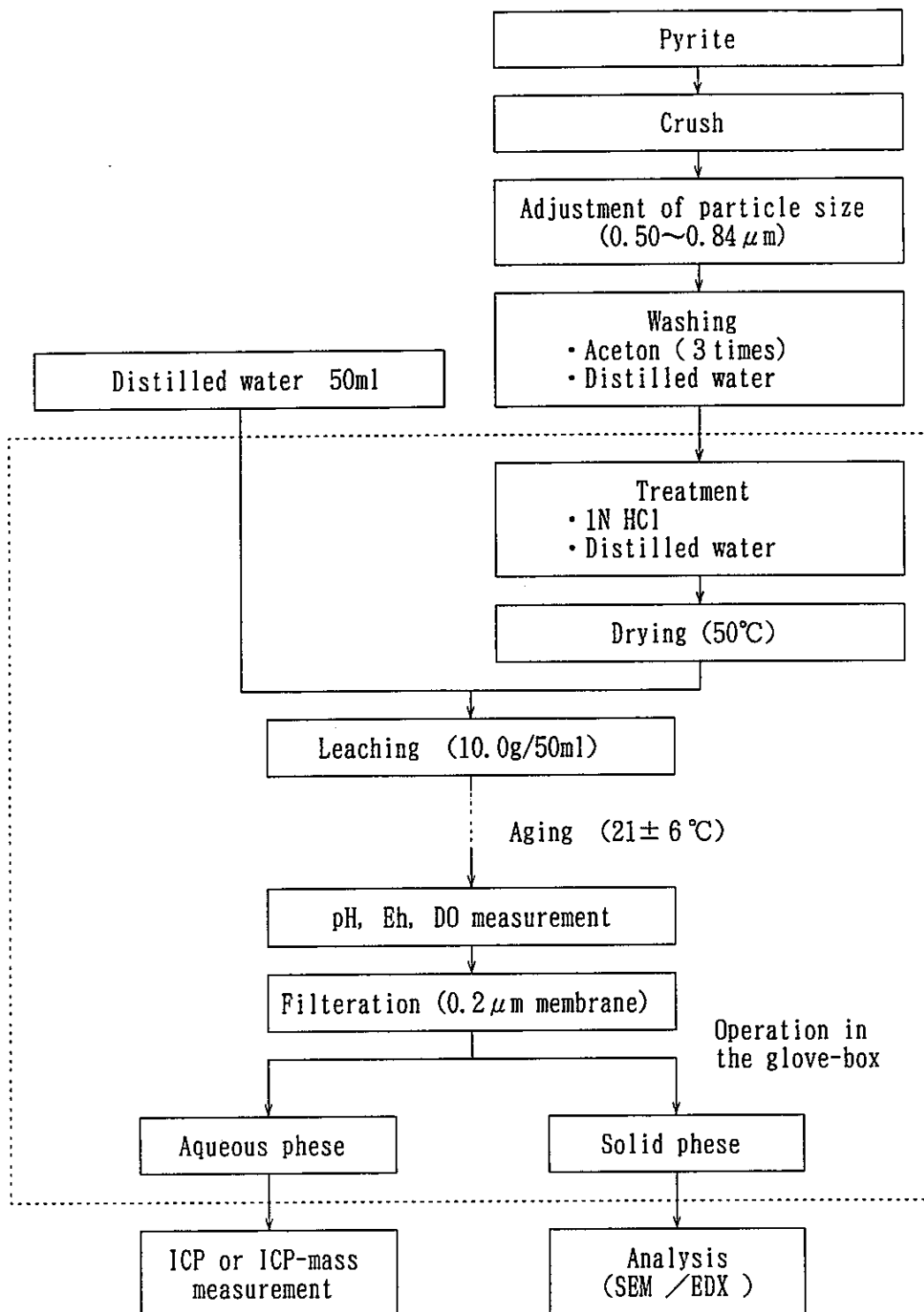


Figure 2.1.1 (2) Flow chart of leaching test for pyrite
(distilled water in equilibrium with air)

2.1.2 Result

(1) Leaching test

Results of leaching test were shown in figure 2.1.2 (1)~(4). p_e was calculated by the equation as follows.

$$p_e = [F / (2.303 \cdot R \cdot K)] \cdot E_h \quad (2.1.1)$$

F : Faraday's constant (96500 c/mol)

R : gas constant (8.31 J/mol/K)

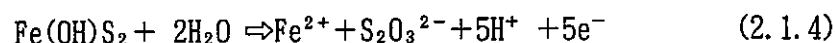
K : absolute temperature

E_h : redox potential (mV)

In the case of reduced distilled water and distilled water in equilibrium with air, redox potential was reducing by progress of leaching reaction.

Congruity of behavior between Fe and S was not observed.

Osseo-Asare¹⁾ was indicated dissolve reaction of pyrite as follows.



In these reaction, It is predicted that redox potential will be reducing by leaching reaction. And pH will be reducing, because of released H^+ ion.

In result of leaching test, redox potential agreed to the prediction, butp H increased reversely. Because H^+ ion was reduced to H_2 gas by released e^- , H^+ would not effect on pH. The occurrence of gas was observed in leaching test really.

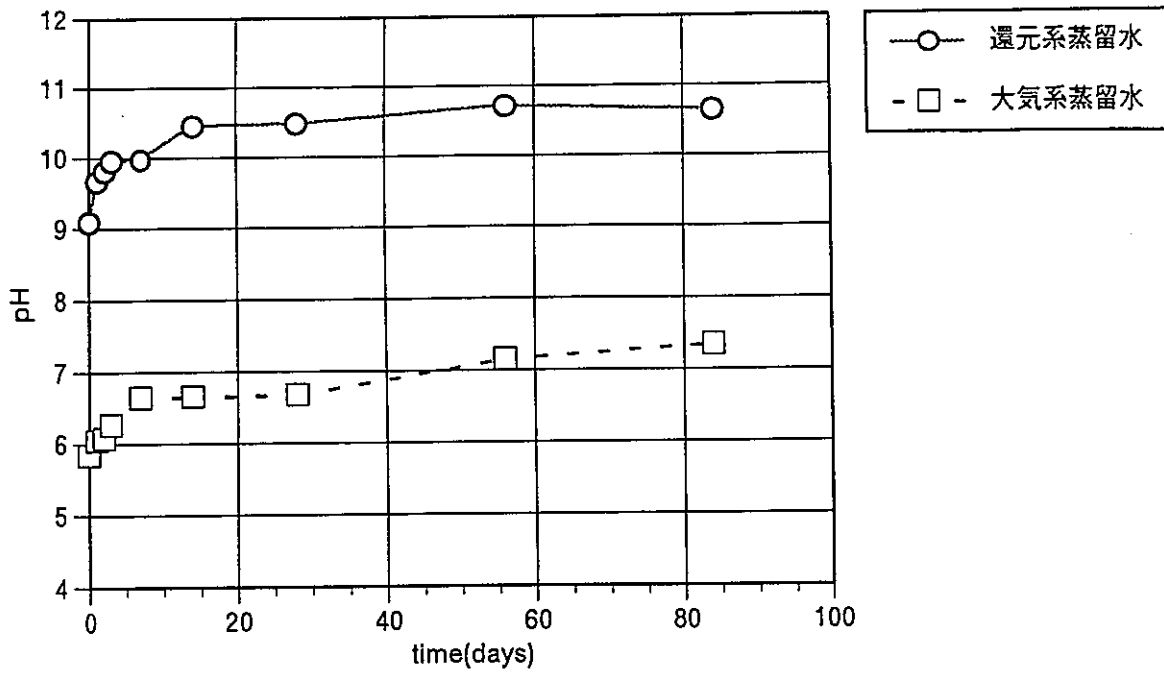


Figure 2.1.2(1) pH depend on leaching time for pyrite

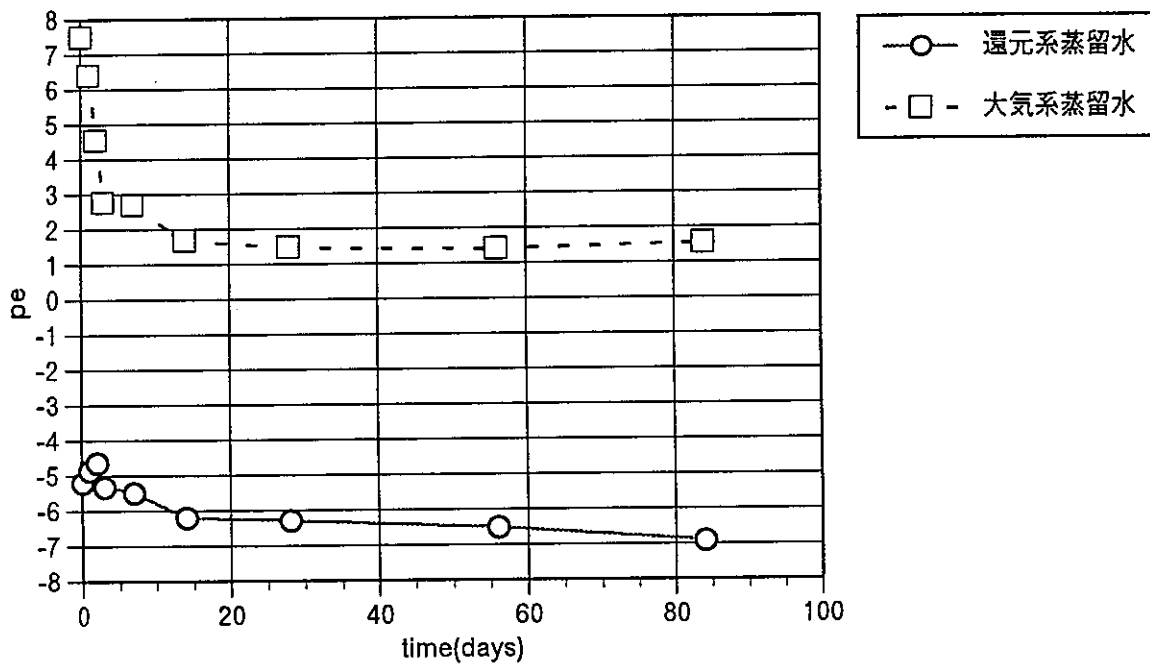


Figure 2.1.2(2) pe depend on leaching time for pyrite

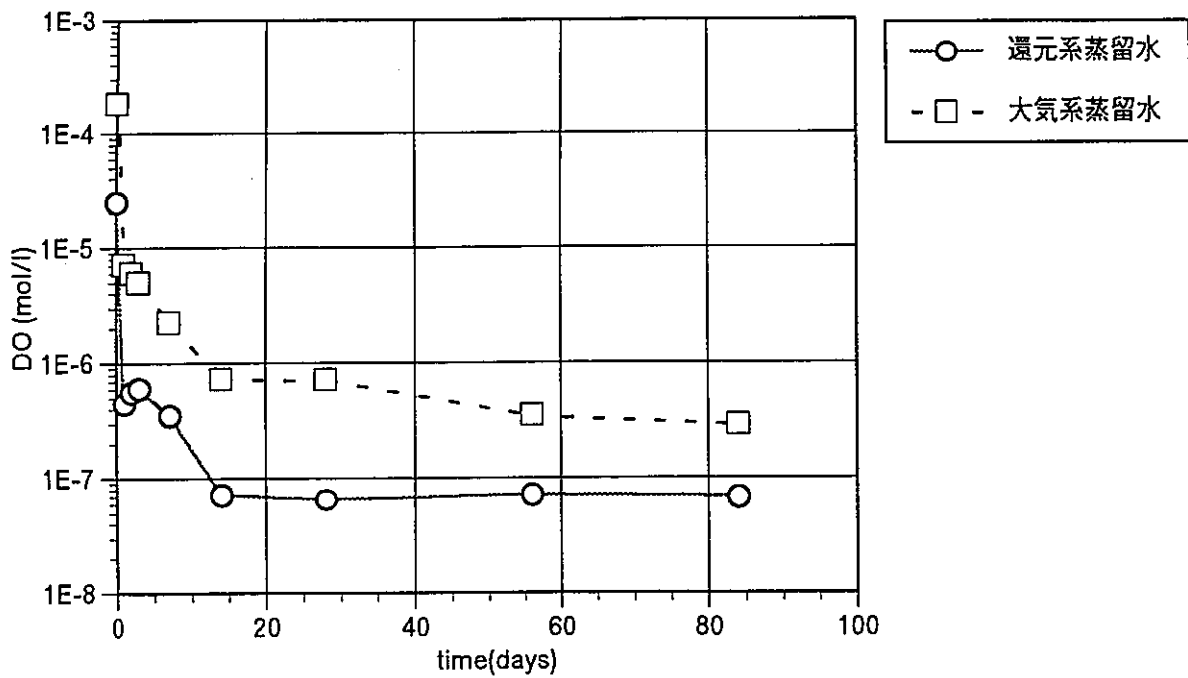


Figure 2.1.2(3) Do depend on leaching time for pyrite

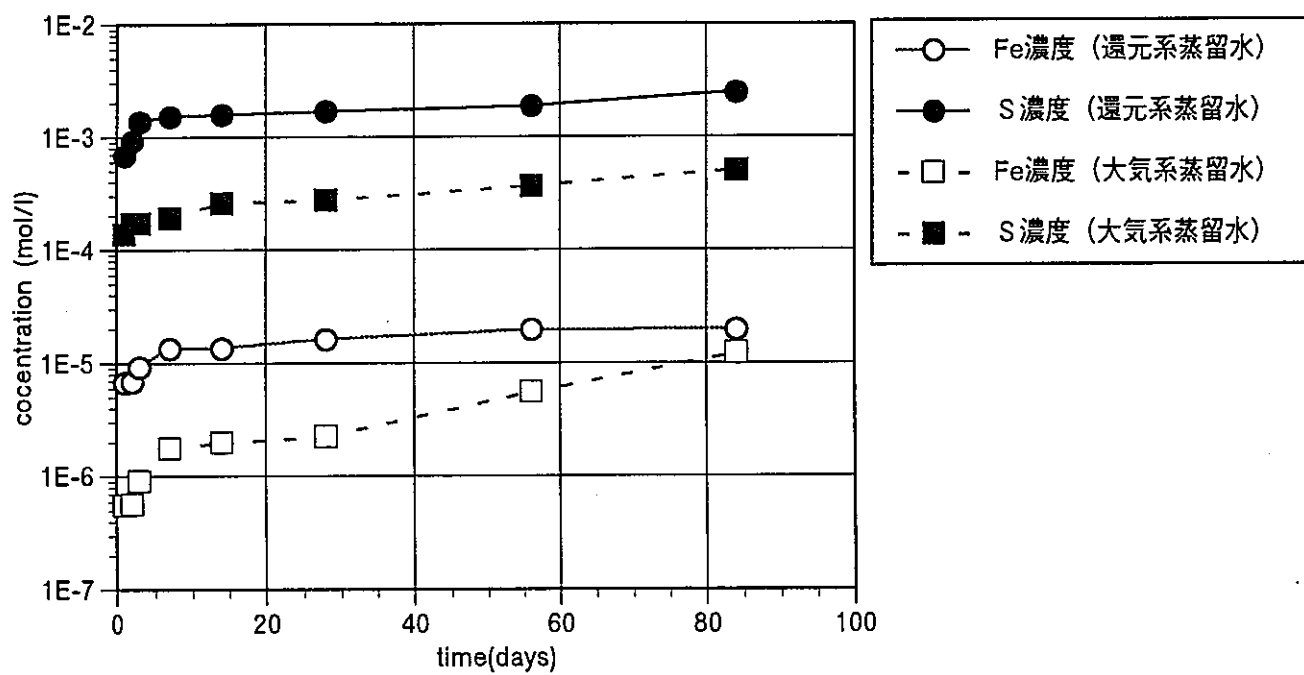


Figure 2.1.2(4) Fe and S depend on leaching time for pyrite

(2) Surface analysis

(a) SEM

After the leaching test, surface of pyrite samples were observed by SEM. In the case of reduced distilled water and distilled water in equilibrium with air, the alteration was not observed.

(b) EDX

After the leaching test, distribution of Fe and S along depth direction of samples were observed by EDX.

The change of concentration was not observed.

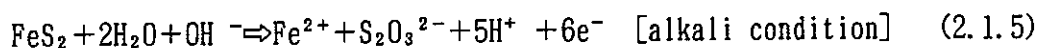
2.1.3 Discussion of leaching rate

(1) Reduced distilled water

The equation of leaching rate is not known in reduced solution.

Solubility product would be estimated in used reaction by Osseo-Asare¹⁾.

Osseo-Asare's reaction was follows.



The solubility product was estimated by equations 2.1.6 ~2.1.7.

$$K = \frac{(\text{Fe}^{2+}) (\text{S}_2\text{O}_3^{2-}) (\text{H}^+)^5 (\text{e}^-)^6}{(\text{FeS}_2) (\text{H}_2\text{O})^2 (\text{OH}^-)} = \frac{(\text{Fe}^{2+}) (\text{S}_2\text{O}_3^{2-}) (\text{H}^+)^5 (\text{e}^-)^6}{(\text{OH}^-)} \quad (2.1.6)$$

$$\begin{aligned} \text{Log } K &= \text{Log}(\text{Fe}^{2+}) + \text{Log}(\text{S}_2\text{O}_3^{2-}) + 5\text{Log}(\text{H}^+) + 6\text{Log}(\text{e}^-) - \text{Log}(\text{OH}^-) \\ &= \text{Log}(\text{Fe}^{2+}) + \text{Log}(\text{S}_2\text{O}_3^{2-}) - 5\text{pH} - 6\text{pe} - (\text{pH} - 14) \\ &= \text{Log}(\text{Fe}^{2+}) + \text{Log}(\text{S}_2\text{O}_3^{2-}) - 6\text{pH} - 6\text{pe} + 14 \end{aligned} \quad (2.1.7)$$

() means concentration (mol/ℓ)

The solubility product (Log K) was estimated to -16.4 in reduced distilled water.

(2) Distilled water in equilibrium with air

Lin et al.²⁾ indicated equation of leaching rate in the presence of oxygen as follows.

$$1 - (1 - x)^{1/3} = k [O_2]^{1/2} t \quad (2.1.8)$$

X : mol amount of dissolve FeS₂
 [O₂] : dissolve O₂ concentration
 t : leaching time
 k : leaching rate

Relation of $1 - (1 - X)^{1/3}$ and $[O_2]^{1/2} \cdot t$ was shown in figure 2.1.3 (1)~(2).

Amount of dissolve FeS₂ was estimated from concentration of Fe and S.

Leaching rates were calculated by equation of 2.1.8, and were shown in table 2.1.2.

In case of distilled water in equilibrium with air, leaching rate was estimated 1.0×10^{-4} and $3.9 \times 10^{-3} \text{ (cm}^3/\text{mol)}^{1/2}/\text{h}$ from concentration of Fe and S respectively. These data were agree with Lin's data²⁾ nearly.

Table 2.1.3 Calculated reaction rate of pyrite by Lin's equation

Solution	Reaction rate k (cm ³ /mol) ^{1/2} /h		
	Measured data		Data by Lin et. ²⁾
Distilled water in equilibrium with air	Estimated by Fe	$(1.0 \pm 0.1) \times 10^{-4}$	8.21×10^{-3} (75°C) 2.54×10^{-2} (90°C)
	Estimated by S	$(3.9 \pm 0.5) \times 10^{-3}$	1.1×10^{-4} (25°C) *

± : Standard deviation (1 σ)

* : The estimation value by Lin's equation [$k = 2.2 \times 10^9 \exp(-9140/T)$]

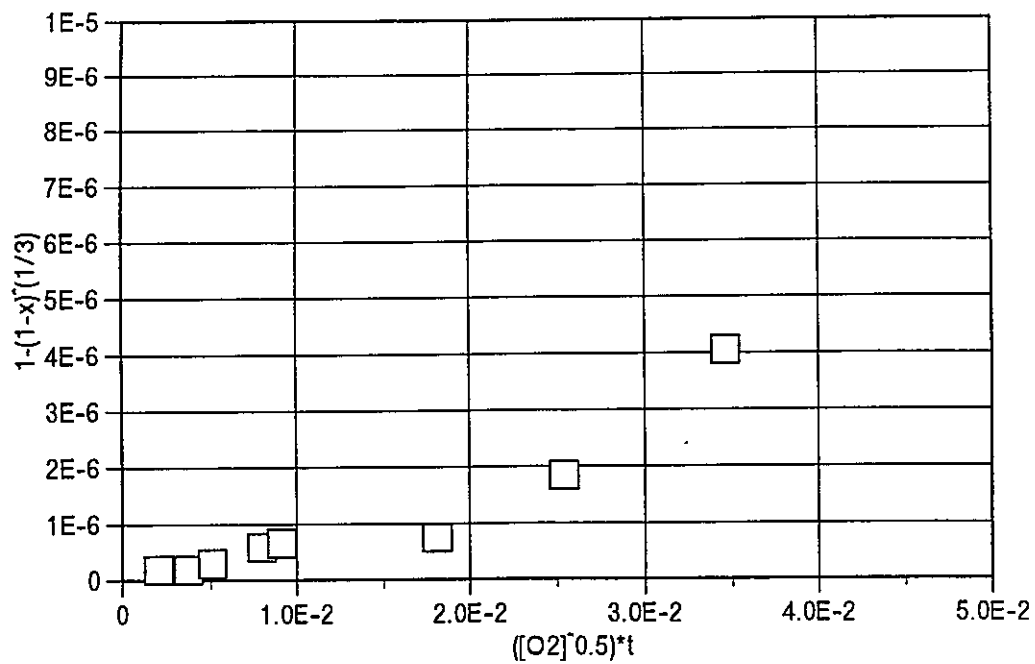


Figure 2.1.3(1) Relation of $[1-(1-x)^{1/3}]$ and $[(O_2)^{1/2} \cdot t]$ (Fe)

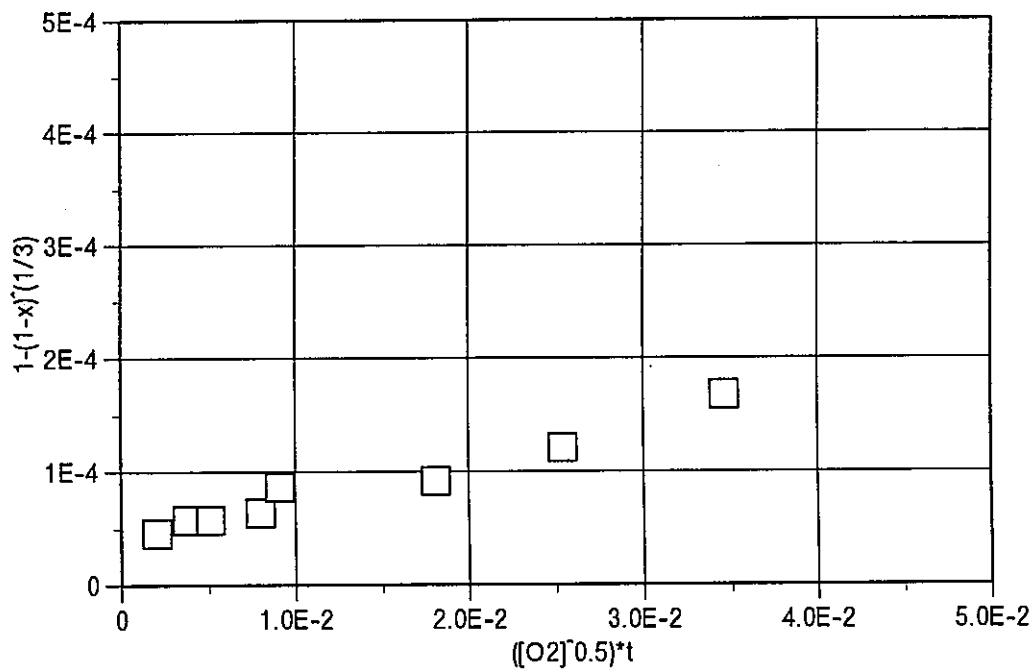


Figure 2.1.3(2) Relation of $[1-(1-x)^{1/3}]$ and $[(O_2)^{1/2} \cdot t]$ (S)

2.2 Measurement of leaching rate of chlorite

Two kind of solution samples were prepared. One was distilled water, another was distilled water that was adjusted pH3.

2.2.1 Experimental method

(1) Sample

(a) Chlorite

Chlorite sample was obtained from Motoyama-chyou(Kochi, Japan).

Elemental composition of sample was shown in table 2.2.1.

Table 2.2.1 Elemental composition of chlorite sample

(wt-%)

element	ratio
Na ₂ O	0.04
K ₂ O	0.04
MgO	32.90
CaO	0.43
Al ₂ O ₃	10.62
FeO	6.45
SiO ₂	31.40
合計	81.88

(b) Distilled water

Distilled water was bought from Waco chemicals co.

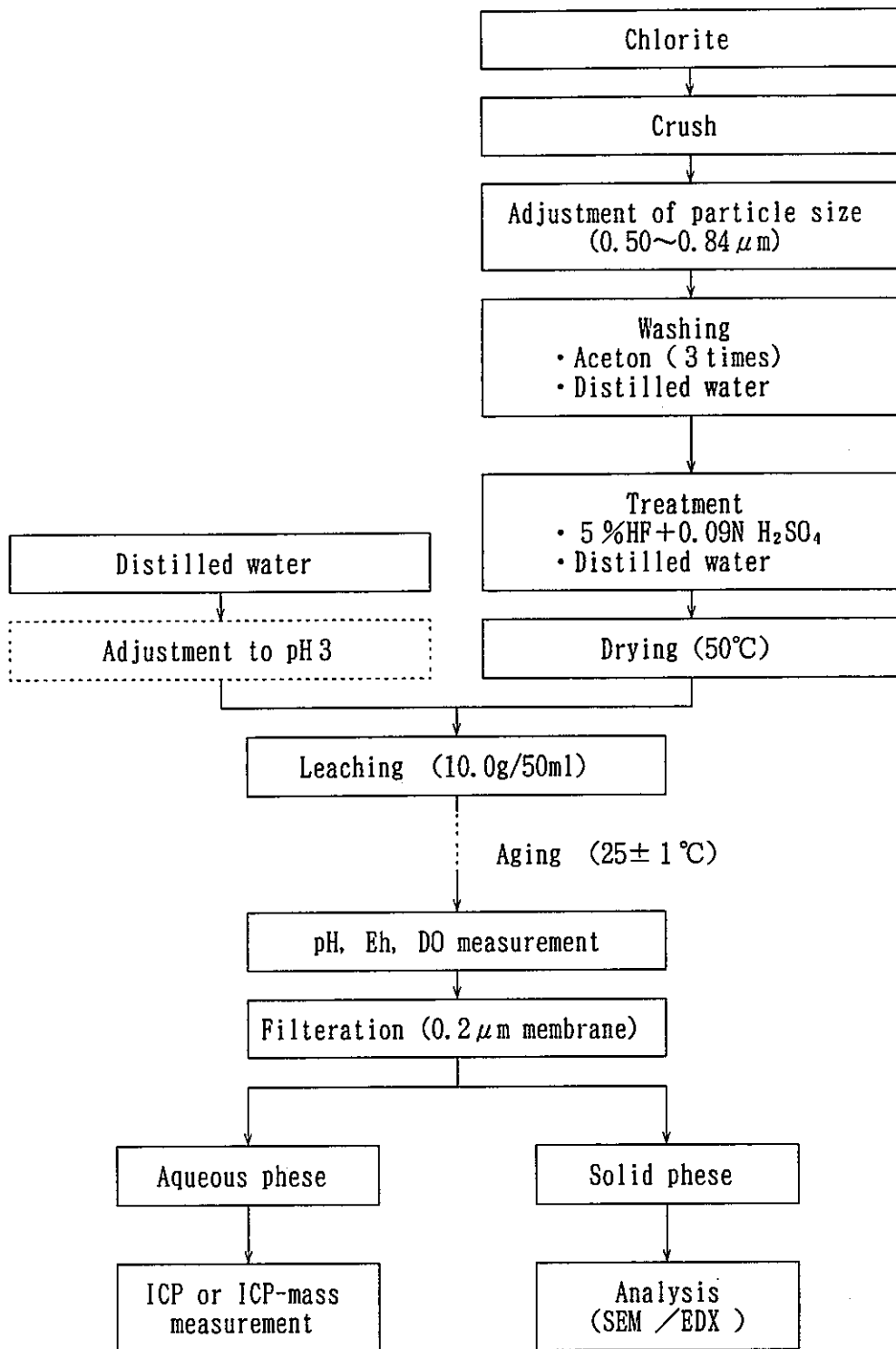


Figure 2.2.1 Flow chart of leaching test for chlorite

2.2.2 Result

(1) Leaching test

Results of leaching test were shown in figure 2.2.2 (1)~(3). All data of Al were lower than detection limit. p_e was calculated by the equation as follows.

$$p_e = \left[F / (2.303 \cdot R \cdot K) \right] \cdot E_h \quad (2.2.1)$$

F : Faraday's constant (96500 c/mol)
R : gas constant (8.31 J/mol/K)
K : absolute temperature
E_h : redox potential (mV)

Initial pH of distilled water and pH3 distilled water were 5.83 and 2.93 respectively.

In both case, pH was increasing by progress of leaching reaction.

In the case of pH3, changing value of pH was larger than that in distilled water.

The difference of Mg and Si concentration were little between distilled water and pH3 distilled water.

(2) Surface analysis

(a) SEM

After the leaching test, surface of chlorite sample was observed by SEM.

In the case of pH3 distilled water, the alteration was not observed.

(b) EDX

After the leaching test, distribution of Mg, Al and Si along depth direction of samples were observed by EDX. The change of concentration was not observed.

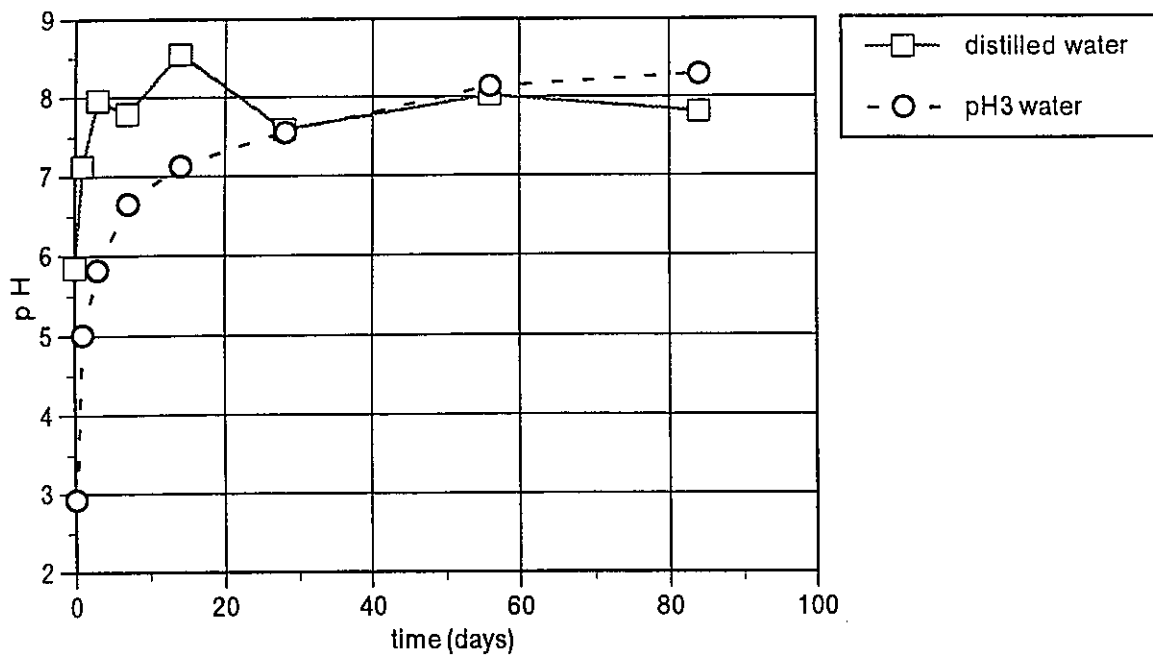


Figure 2.2.2(1) pH depend on leaching time for chlorite

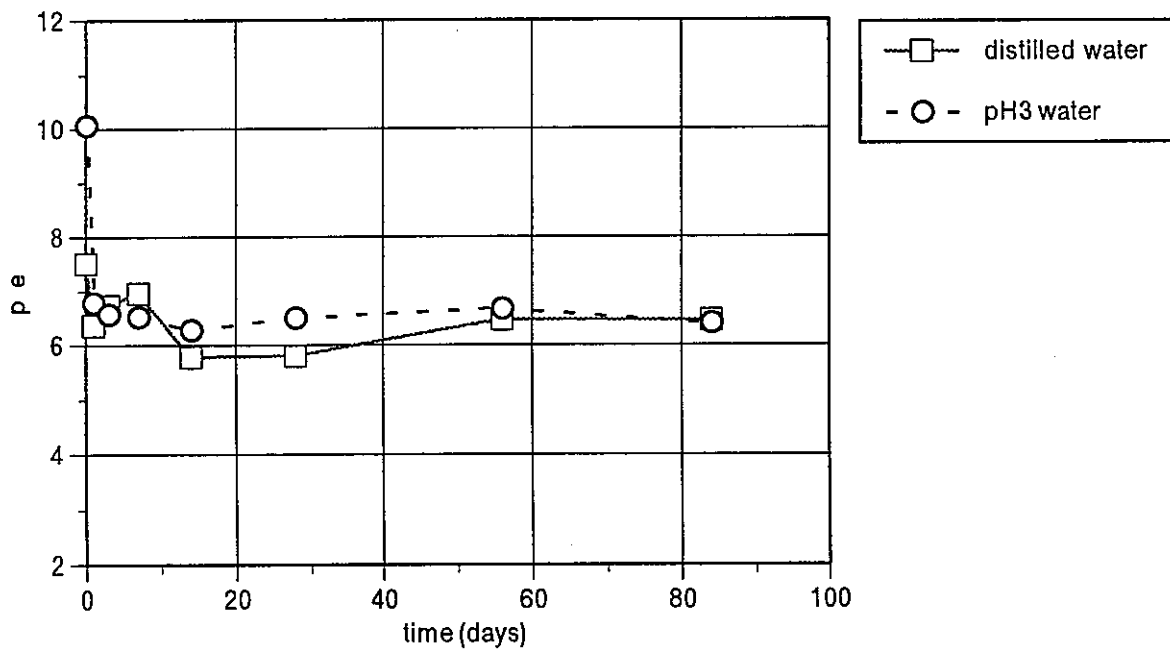


Figure 2.2.2(2) pe depend on leaching time for chlorite

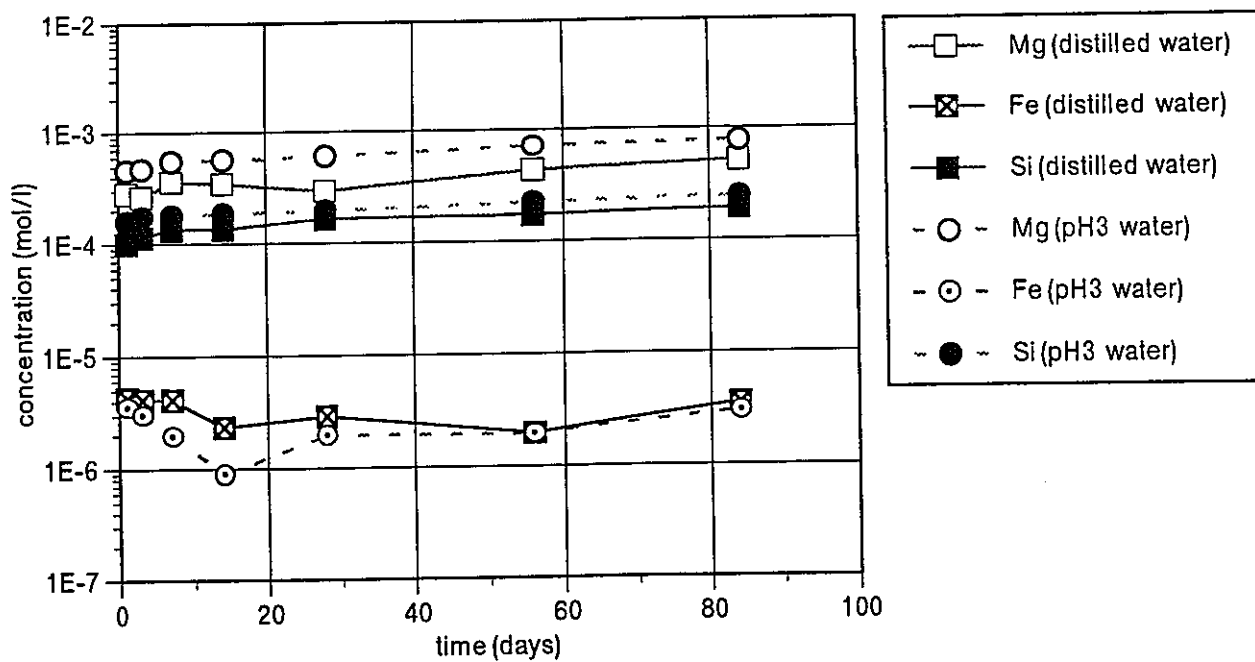


Figure 2.2.2(3) Mg,Fe,Si depend on leaching time for chlorite

2.2.3 Discussion of leaching rate

Ross³⁾ are indicated dissolve reaction of chlorite as follows.

$$\alpha^2 = k t \quad (2.2.2)$$

α : ratio of dissolve amount and initial amount
 k : leaching rate
 t : leaching time

leaching rate(K) was estimated by used equation 2.2.2.

α value was calculated from elemental composition in table 2.2.1.

Relation of α^2 and leaching time(t) was shown in figure 2.2.3(1)~(2).

Leaching rate were calculated by equation of 2.2.1. and were shown in table 2.2.3.

In case of distilled water and pH3 distilled water, leaching rate was estimated $10^{-15} \sim 10^{-14}$ from concentration of Mg and Si respectively.

Table 2.2.3 Estimated reaction rate(K_1) of chlorite by α^2

Solution	Estimated by Mg	Estimated by Si
Distilled water(pH 5.85)	$(9.3 \pm 1.7) \times 10^{-15}$	$(3.1 \pm 0.4) \times 10^{-15}$
Distilled water(pH 2.93)	$(2.1 \pm 0.2) \times 10^{-14}$	$(4.2 \pm 0.2) \times 10^{-15}$

\pm : Standard deviation (1σ)

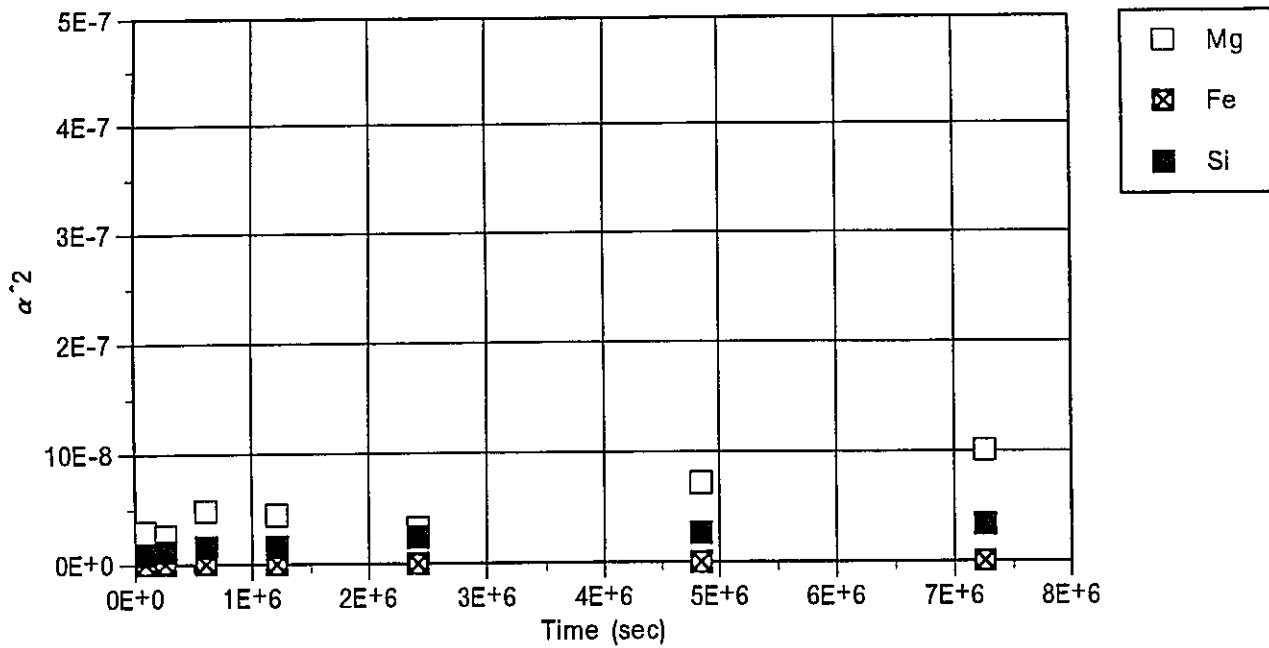


Figure 2.2.3(1) Relation of α^2 and leaching time (distilled water)

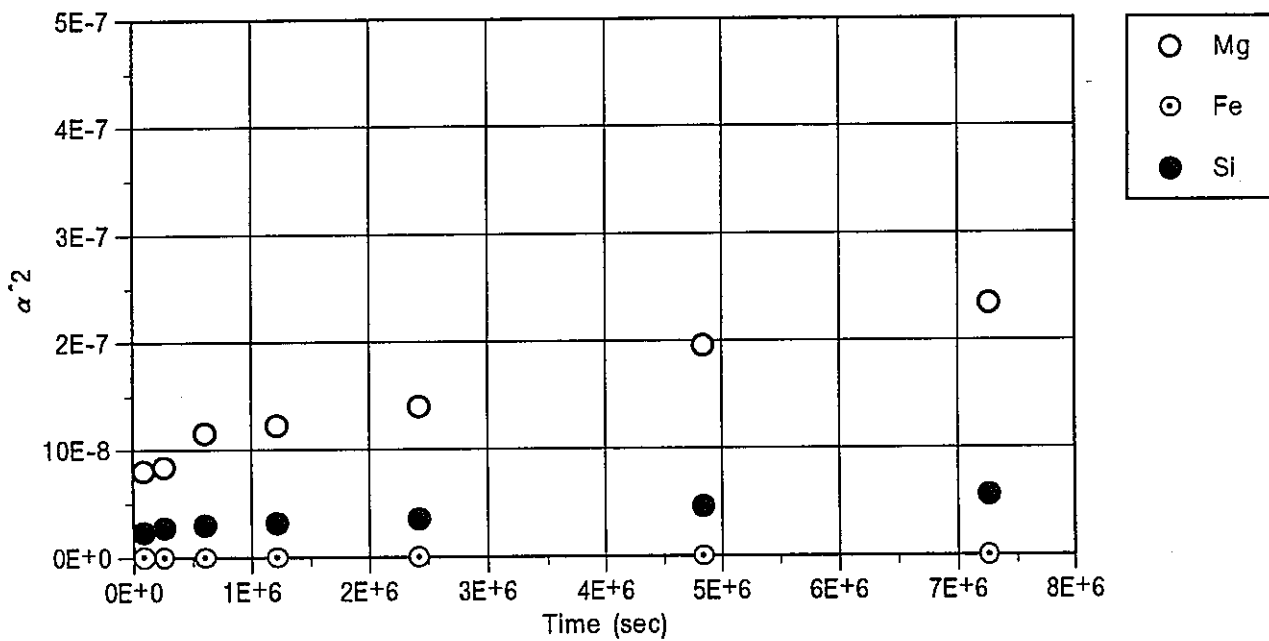


Figure 2.2.3(2) Relation of α^2 and leaching time (pH3 distilled water)

Reference)

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