

# EFFECT OF OXYGEN SPARGING INTO PACKED-BED ELECTRODE ON PRODUCTION RATE OF HYDROGEN PEROXIDE

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**Key Words:** Electrolysis, Hydrogen Peroxide, Packed-Bed Electrode, Oxygen Sparging, Energy Consumption

Production of hydrogen peroxide by electroreduction of oxygen in alkaline solutions was experimentally carried out using a packed-bed electrode of graphite particles or graphite felts. Oxygen sparging into the bed was found to increase overall yield of hydrogen peroxide for a one-pass operation because of the increase in concentration of dissolved oxygen. The current efficiency decreased with increasing concentration of hydrogen peroxide. Effects of packing materials, sparging rate of oxygen and operational conditions on production rate were analysed by measuring potential distribution within the bed. The production rate for the electrolysis using graphite felts was found to be larger than that using graphite particles. The felt cathode had a large electrode surface area and a large volumetric ratio of gas to electrolyte, which might enhance the mass transfer rate of dissolving oxygen. The consumption of electric power for producing hydrogen peroxide was found to range from 2 to 6 kWh·kg<sup>-1</sup>-H<sub>2</sub>O<sub>2</sub> in the packed-bed electrode with graphite felts.

## Introduction

Hydrogen peroxide was produced through electroreduction of oxygen in alkaline solution, as reported in previous papers.<sup>9,10)</sup> Since the electrolyte was recycled from the oxygen absorber to the packed bed, the production rate of hydrogen peroxide was affected by rates of oxygen sparging and electrolyte flow. Polarization characteristics of the packed-bed electrode reactor were clarified by using a two-dimensional, two-phase model of the particulate

electrode. When the reaction is carried out in a continuous operation, direct sparging of oxygen into the reactor is required in order to maintain the concentration of dissolved oxygen in the solution. Since the concentration of the reactant, *i.e.*, the dissolved oxygen, was lower than that for an ordinary electrolysis, a three-dimensional electrode<sup>8)</sup> such as a packed-bed electrode was desired to increase the production rate in the reactor. Oloman *et al.*<sup>6,8)</sup> presented a tricklebed electrochemical reactor. Oxygen gas and the electrolyte flow cocurrently downward through the packed cathode bed of graphite particles. Brown *et al.*<sup>1)</sup> used composite chips of Teflon latex and carbon black coated on graphite particles to

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obtain sufficient porosity because of the water repellency of Teflon. The gas phase in the bed decreases the effective conductivity of the electrolyte phase in the bed but the turbulent motion of the bubbles enhances the liquid-solid mass transfer of the interface of a particulate electrode<sup>3)</sup>.

The objective of this paper is to clarify the effect of oxygen sparging into a packed-bed electrode of graphite particles or felts on the production rate of hydrogen peroxide.

## 1. Experimental

Figure 1 shows an experimental apparatus similar to that described in the previous paper<sup>9)</sup>. The feeder electrode was 5 cm × 10 cm in dimensions. The bed depth, *i.e.*, the distance from the feeder to the separator, was 1 cm, 5 mm or 2 mm. Three kinds of graphite particles (GP-A: crushed particles 1.7 mm in mean diameter; GP-B and C: cylindrical particles specially molded by Tokai Carbon Co., 3 mmφ × 3.6 mm, and 2 mmφ × 2.1 mm respectively), and also graphite felt (Nippon Carbon, GF-20) were employed as packing materials. The catholyte was a mixture of 1 kmol · m<sup>-3</sup> KCl and 0.01 kmol · m<sup>-3</sup> NaOH solution and the anolyte was a 1 kmol · m<sup>-3</sup> NaOH solution. The electrolyte was cooled to 288 K by passing a coolant in a reservoir and by immersing a cooling coil in the upper part of the reactor above the packed bed. Oxygen gas or air was sparged by three pipes of stainless steel, 1.7 mm in inner diameter, from the lower part of the reactor. The electrolyte at the reactor outlet in steady-state operation was sampled to determine the concentration *C<sub>p</sub>* of the peroxide. The potential distribution in the bed was measured by a Luggin capillary inserted from the back of the feeder electrode. The superficial velocities of gas and electrolyte, *u<sub>G</sub>* and *u<sub>L</sub>*, ranged from 0.8 cm · s<sup>-1</sup> to 10.2 cm · s<sup>-1</sup>, and from 5 × 10<sup>-3</sup> cm · s<sup>-1</sup> to 5 × 10<sup>-2</sup> cm · s<sup>-1</sup>, respectively. Electrolysis procedures were the same as those described previously.<sup>9)</sup>

## 2. Results and Discussion

### 2.1 Peroxide concentration

Figure 2 shows the relationship between the current density, *i*, based on the surface area of the feeder electrode and the cathodic potential, *E*, vs. Ag/AgCl reference electrode. The current density in the packed-bed electrode was larger by an order of magnitude than that for electrolysis with a planar feeder electrode. The stepwise curve<sup>10)</sup> of the current density-potential relationship characteristic of successive and competitive reactions in the electroreduction of oxygen in alkaline solution was not evident for the packed-bed electrode. This was due to the fact that the potential distribution was formed through the bed depth<sup>9)</sup>. The *i* value at *u<sub>G</sub>* = 6.6 cm · s<sup>-1</sup> was larger

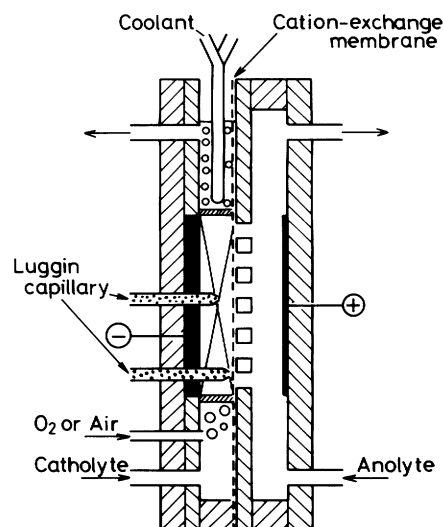


Fig. 1. Schematic diagram of packed-bed electrode reactor

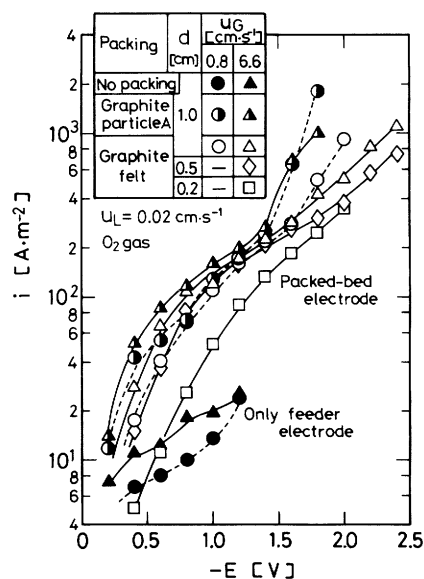


Fig. 2. Relationship between current density and cathodic potential for different packings and operating conditions

than that at *u<sub>G</sub>* = 0.8 cm · s<sup>-1</sup> when *E* was less negative than -1.5 V. Since oxygen sparging was considered to decrease the electrolyte conductivity, *i* had the tendency to decrease with increasing *u<sub>G</sub>* at *E* < -1.5 V. The current density increased with increasing bed depth.

Properties of different packing materials are listed in Table 1. The value of *i* became large in the order of the smaller particles, GP-B, GP-C and GP-A and the value of *i* of the felt cathode was close to that of the GP-A cathode. The effect of packing materials will be discussed in detail below.

The current efficiency *C<sub>e</sub>* we calculated according to the following equation:

$$C_e = \frac{2FC_P Q_L}{I} \times 100\% \quad (1)$$

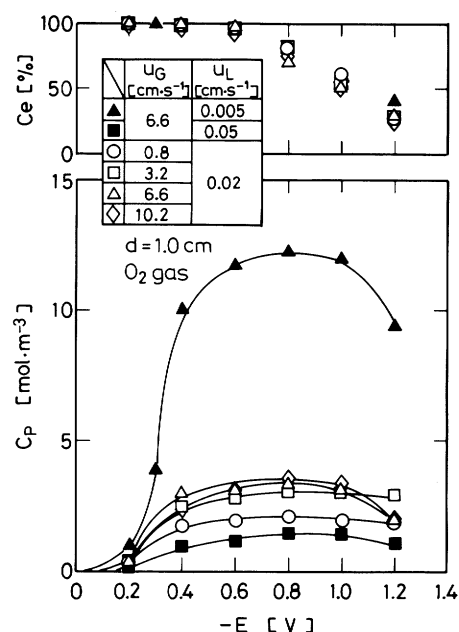
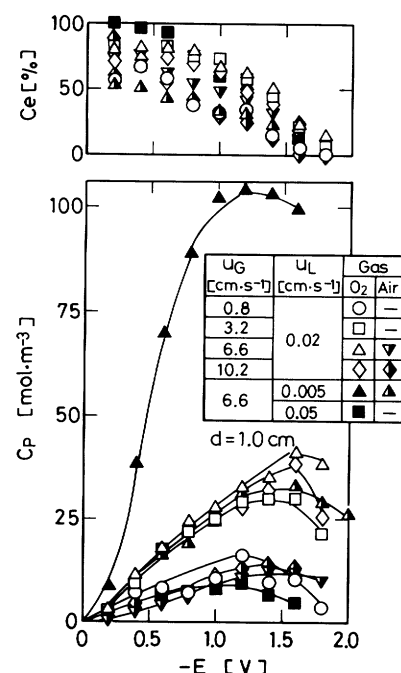
**Table 1.** Properties of packed beds

Packing material		$d$ [mm]	$d_{pv}$ [mm]	$W \times 10^3$ [kg]	$\varepsilon_s$ [—]	$a \times 10^{-3}$ [m <sup>-1</sup> ]
Graphite particles	A	10	1.7	61	0.69	2.44
	B	10	3.7	55	0.61	0.99
	C	10	2.3	55	0.61	1.59
Graphite felts		10	0.015	6.8	0.076	30.4
		5	0.015	3.4	0.076	30.4
		2	0.015	1.2	0.067	26.8

**Figure 3** shows the peroxide concentration for the electrolysis at different potentials when only a feeder electrode is employed. The peroxide concentration maximized at  $-0.8$  V of cathodic potential  $E$ . The current efficiency was almost 100% in the more positive range and decreased at a potential  $E$  more negative than  $-0.4$  V. **Figure 4** shows the peroxide concentration for the electrolysis at different potentials in the packed-bed electrode of graphite particles A. The peroxide concentration increased with decreasing  $u_L$ . When  $u_L$  was  $0.02 \text{ cm} \cdot \text{s}^{-1}$ ,  $C_P$  at a  $u_G$  value of  $6.6 \text{ cm} \cdot \text{s}^{-1}$  was higher than the others. When air was sparged instead of oxygen gas, the peroxide concentration was decreased to one-fourth the  $C_P$  value when using oxygen gas. The peroxide concentration maximized at about  $-1.0$  V, a more negative potential than the  $-0.8$  V for planner feeder electrode, as depicted in Fig. 3. The current efficiency decreased with increasing negative cathodic potential. When air was sparged,  $C_e$  was lower than that for oxygen gas. **Figure 5** shows the peroxide concentration for the electrolysis at different potentials in the packed-bed electrode of graphite felts. Current efficiency when using the felt cathode was higher than that when using the particle cathode depicted in Fig. 4. When the bed depth  $d$  was decreased, the peroxide concentration increased. This was due to the fact that the current concentration increased with decreasing  $d$ . From the numbers in Fig. 2, current concentrations at  $E = -1.6$  V were calculated to be  $26 \text{ kA} \cdot \text{m}^{-3}$ ,  $50 \text{ kA} \cdot \text{m}^{-3}$  and  $90 \text{ kA} \cdot \text{m}^{-3}$  for  $d = 1.0$  cm,  $0.5$  cm and  $0.2$  cm respectively. Peroxide of concentration higher than 1% ( $294 \text{ mol} \cdot \text{m}^{-3}$ ) was obtained experimentally but  $C_e$  decreased with increasing concentration of peroxide.

## 2.2 Gas holdup in packed bed

To clarify the effect of packing materials on current efficiency, the potential distribution in the bed was measured. **Figure 6** shows the difference in potential between the electrolyte phase and the matrix phase at various depths in the bed. The potential  $\phi_M$  of the matrix phase was constant through the bed. The potential difference  $\phi_s - \phi_M$  was equal to  $-E$  at the separator ( $x = 0$ ) and decreased with increasing bed depth  $x$  from the separator. The decreasing gradient

**Fig. 3.** Current efficiency and peroxide concentration produced using graphite plate cathode**Fig. 4.** Current efficiency and peroxide concentration produced in packed-bed cathode of graphite particles A

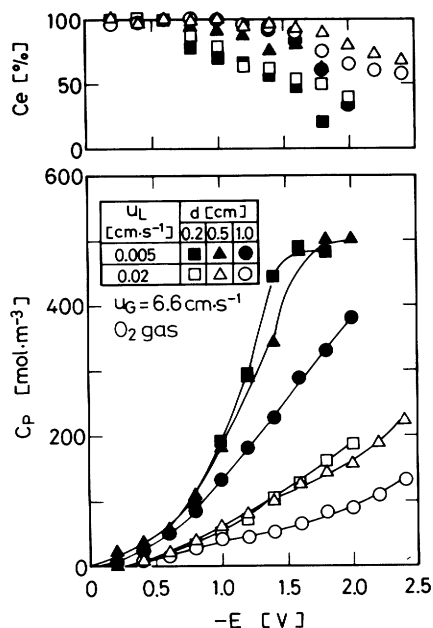


Fig. 5. Current efficiency and peroxide concentration produced in packed-bed cathode of graphite felts

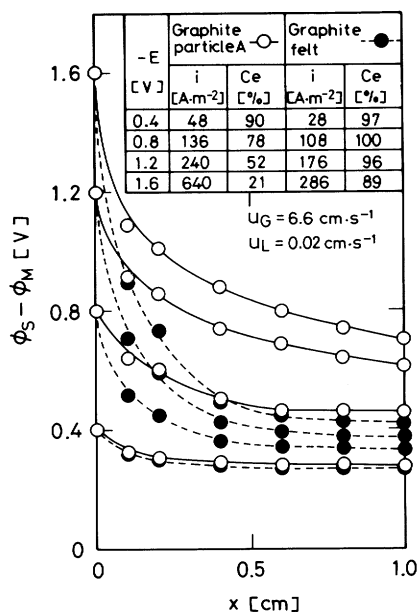


Fig. 6. Cathodic potential profiles in packed-bed electrodes of graphite particles and felts

of the potential in the felt cathode in the vicinity of the separator was larger than that in the bed of GP-A. To compare electrolysis properties using GP-A and the felts, the relationship among  $E$ ,  $i$  and  $Ce$  are depicted in Fig. 6. Especially at the more negative potential,  $i$  in the felt cathode was lower than that in the particle cathode but  $Ce$  using the felt cathode was higher than that using the particle cathode. Figure 7 shows the gradient of the electrolyte potential at  $x = 0.1$  in the vicinity of the separator at different currents. According to a two-phase model of a particulate electrode,<sup>5,11)</sup> Ohm's law in the electrolyte is

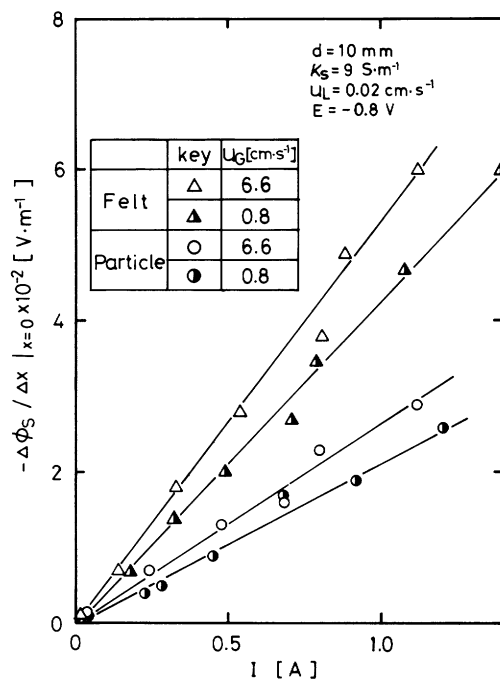


Fig. 7. Relationship between potential gradient near separator and electric current

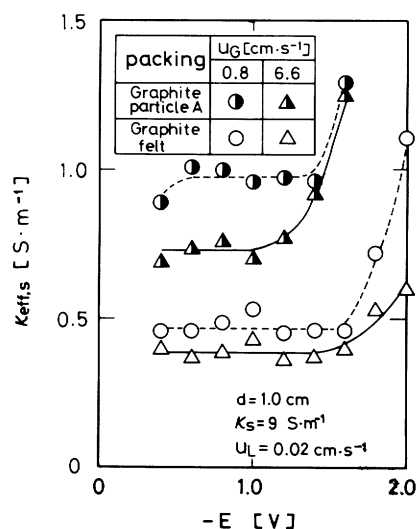


Fig. 8. Effective conductivities of electrolyte for different packed-bed electrodes

expressed as follows.

$$i_S = -\kappa_{eff,s} \nabla \phi_S \quad (2)$$

Gradients of the potential of the electrolyte with respect to bed depth were linearly proportional to currents. At the separator ( $x = 0$ ),  $i_S$  is equal to the total current  $i$ . From the slope of the potential difference relative to the current density as depicted in Fig. 7,  $\kappa_{eff,s}$  was obtained. Figure 8 shows  $\kappa_{eff,s}$  obtained at different potentials when GP-A and the felts were employed. The values of  $\kappa_{eff,s}$  showed the constants at a potential more negative than  $-1.2 \text{ V}$ . Since the gradient of the potential became large with

**Table 2.** Electrolysis properties using different packings;  $d=1\text{ cm}$ ,  $E=-1.0\text{ V}$ ,  $u_L=0.02\text{ cm}\cdot\text{s}^{-1}$  and  $u_G=6.6\text{ cm}\cdot\text{s}^{-1}$ 

Packing material		$i\text{ [A}\cdot\text{m}^{-2}\text{]}$	$C_P\text{ [mol}\cdot\text{m}^{-3}\text{]}$	$Ce\text{ [\%]}$	$\varepsilon_L\text{ [—]}$	$\varepsilon_G\text{ [—]}$
Graphite particles	A	160	28	68	0.19	0.12
	B	115	19	64	0.23	0.16
	C	120	20	64	0.18	0.21
Graphite felts		158	40	98	0.12	0.804

increasing current density, the estimation error using the gradient at  $x=0.1$  was considered to be large at a potential less negative than  $-1.2\text{ V}$ .

If Bruggeman's relationship<sup>2)</sup> is applicable to the electrolyte phase, the holdup of the electrolyte  $\varepsilon_L$  is expressed as follows.

$$\varepsilon_L = (\kappa_{eff,S}/\kappa_S)^{-1/1.5} \quad (3)$$

The holdup  $\varepsilon_S$  of the solid phase of the electrode was estimated from the weight of the particles or felts packed in the cell.

$$\varepsilon_S = W/(\rho_p V) \quad (4)$$

where  $\rho_p$  is the density of the graphite, assuming to be  $1.78 \times 10^3\text{ kg}\cdot\text{cm}^{-3}$ .

The surface area  $a$  of electrode per unit volume was estimated as follows.

$$a = \frac{6\varepsilon_S}{d_{pv}} \quad (5)$$

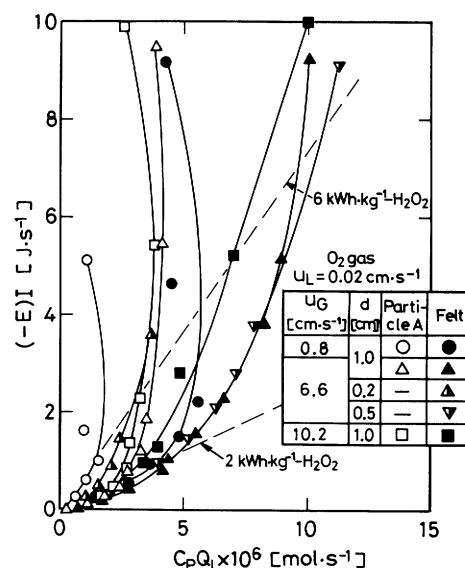
The values of  $\varepsilon_S$  and  $a$  of different packings are listed in Table 1. Using  $\varepsilon_L$  and  $\varepsilon_S$ , the holdup  $\varepsilon_G$  of the gas phase in the bed was

$$\varepsilon_G = 1 - \varepsilon_S - \varepsilon_L \quad (6)$$

Comparison among electrolysis properties, and holdups of liquid and gas using different packings, are listed in Table 2. The  $\kappa_{eff,S}$  value of the felt cathode was lower than that of the particles because gas bubbles were considered to attach to and remain behind the network structure of the felts. The  $\varepsilon_G$  value in the felt cathode was larger than that in the particle cathode. The reason why  $Ce$  and  $C_P$  in the felt cathode were higher than those in the particle cathode, as shown in Table 2, might be the high values of  $a$  and the mass transfer rate of dissolving oxygen by a large volumetric ratio of gas to electrolyte. The large surface area of the felt electrode was confirmed by electrooxidation of ferrous ion in a flow-by packed-bed electrode.<sup>4)</sup>

### 2.3 Power consumption

Figure 9 shows the relationship between the power consumption and production rate of hydrogen peroxide. In the ideal case, ohmic drops of the separator and anodic compartment, and also the anodic potential, can be reduced as much as possible. The power consumption was estimated from the

**Fig. 9.** Relationship between power consumption and production rate of peroxide

cathodic potential and the current for actual electrolysis. Production rates,  $C_P Q_L$ , using graphite particles A and the felts, were approaching the maxima of  $3 \times 10^{-6}\text{ mol}\cdot\text{s}^{-1}$  and  $10 \times 10^{-6}\text{ mol}\cdot\text{s}^{-1}$  respectively. Power consumption per unit kg of hydrogen peroxide produced using GP-A and graphite felts ranged from 2–12 kWh and 2–6 kWh respectively. The presence of gas in a packed-bed electrode increased the cathodic potential by increasing cell resistance and current density, and increased current efficiency by maintaining high concentration dissolved in the electrolyte, as shown in the trickle-bed electrode<sup>5)</sup>. Since the current efficiency dominantly increased by oxygen sparging into the felt cathode, the consumption of electric power per unit kg of hydrogen peroxide was reduced by using a oxygen-sparged felt cathode rather than an oxygen-sparged particle cathode. The power consumption of  $6\text{ kWh}\cdot\text{kg}^{-1}\text{-H}_2\text{O}_2$  was competitive with that of the pressurized trickle-bed cathode<sup>7)</sup>.

### Conclusions

Oxygen sparging into the packed-bed electrode of graphite felts was effective in producing hydrogen peroxide with high current efficiency. A peroxide concentration over 1% was obtained experimentally

but the current efficiency became lower at higher concentration. Holdup of the gas phase in the felt cathode was found to be larger than that in the particulate cathode because the network structure maintains gas bubbles attached behind the felt fibers. Power consumption using the felt cathode ranged from 2 to 6 kWh per unit kg of hydrogen peroxide.

#### Nomenclature

$a$	= surface area of electrode per unit volume	$[\text{m}^{-1}]$
$C_e$	= current efficiency defined by Eq. (1)	$[\%]$
$C_p$	= peroxide concentration	$[\text{mol} \cdot \text{m}^{-3}]$
$d$	= bed depth	$[\text{m}]$
$d_{pv}$	= diameter equivalent to spherical volume	$[\text{m}]$
$E$	= cathodic potential	$[\text{V}]$
$F$	= Faraday's constant	$[\text{C} \cdot \text{mol}^{-1}]$
$I$	= electric current	$[\text{A}]$
$i$	= current density	$[\text{A} \cdot \text{m}^{-2}]$
$Q_L$	= volumetric flow rate	$[\text{m}^3 \cdot \text{s}^{-1}]$
$u$	= superficial velocity	$[\text{m} \cdot \text{s}^{-1}]$
$V$	= volume of packed bed	$[\text{m}^3]$
$W$	= dry weight of packing	$[\text{kg}]$
$x$	= bed depth coordinate	$[\text{m}]$
$\varepsilon$	= holdup	$[-]$
$\phi$	= electric potential	$[\text{V}]$
$\kappa_S$	= electrolyte conductivity	$[\text{S} \cdot \text{m}^{-1}]$
$\kappa_{eff,S}$	= effective conductivity of electrolyte	$[\text{S} \cdot \text{m}^{-1}]$
$\rho_p$	= density of graphite	$[\text{kg} \cdot \text{m}^{-3}]$

#### <Subscripts>

$G$	= gas
$L$	= liquid
$M$	= matrix
$S$	= solution

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(Presented at the Hokuriku Meeting of The Society of Chemical Engineers, Japan at Toyama, July 17, 1986.)