Bull. Shimane Univ. (Natural Sci.) No. 15, pp. 38–45. December, 1965.

# On the Preparations of Magneti Metal-Oxides (I)

(Solubilities of Sand-iron and Spongy-iron in Acids, and their Oxidation by Air-Blow)

SAKUJIRO YAMAMOTO


## Summary

For the preparations of ferric oxide and ferrousferric oxide as the primary materials for ferrite magnets and magnetic metal-oxide for tape recording, the fine sand-iron and the special spongy-iron produced at TORIGAMI BRANCH FACTORY and at the METALLUGICAL LABORATORY of HITACHI-INZOKU Co., YASUGI are used respectively. The distributions of the particle-sizes of sand-iron, the iron contents by each grade of their particle-sizes, the solubilities of sand-iron and spongy-iron in hydrochloric acid and sulphuric acid, and then the effects of temperature on them are fundamentally researched.


## Experiment and Discusstion

〔I〕 Trearments of Sand-iron and spongy-iron with acids.

(1) Sand-iron and spongy-iron used.

Table 1 gives the distribution of particle-sizes of the sand-iron corrected from the River Hii. Fig. 1 and Fig. 2 indicate the iron contents of each particle and their chemical constituents respectively ; it is unexpectedly found so small that about half of the sand-iron has the size range in 200 mesh, and iron contents are rather larger in smaller particles than in larger ones. Iron is measured volumetrically with standardized $N_2S_2O_3$ solution.[1)]

Table 1. Fe in sand-iron by particle-size

| particle-size / Fe | mech 240 | mech 240–200 | mech 180–160 | mech 160–140 | mech 140–120 |
|---|---|---|---|---|---|
| % | 74.0 | 74.0 | 72.6 | 72.6 | 72.6 |

Table 2. Chemical analysis of samples.

| component / sample | T. Fe | FeO | $Fe_2O_3$ | M. Fe | P | S | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | CaO |
|---|---|---|---|---|---|---|---|---|---|---|
| sand-iron | 73.50 | 31.09 | 61.98 | – | 0.100 | Tr. | 1.40 | 3.45 | 0.26 | 1.31 |
| spongy-iron※ | 89.70 | 7.50 | 0.50 | 85.50 | 0.105 | 0.108 | – | 4.85 | – | – |

※ mean values of seven samples

The chemical analysis of spongy. iron is done with samples passed through 100 mesh, of seeve, and its data are given in Table 2.

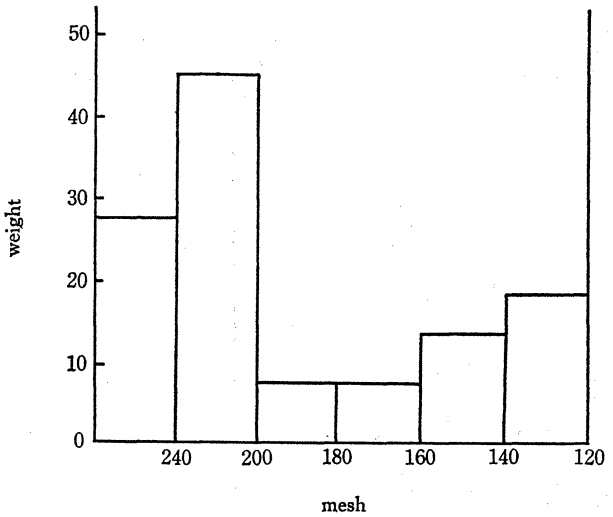


Fig. 1. Distribution of particles of sand-iron

(A) Hydrochloric acid

The Fig. 2—Fig. 5 give their characteristic solubilities of sand-iron and spongy-iron in 4N-and 12N-HCL. Sand-iron, when trieted in 12N-HCL at 100°C for 30 min. and in 4N-HCL at 100°C 30 min., has almost the same solubilities (80%). For spongy-iron, the effects of HCL concentration on the solubilities are remarkable ; in the diluted HCL solution, the solubilities of spongy-iron are smaller than those of sand-iron, but in the concentrated solution, they amount to 96.5% at 100°C for 90 min.,

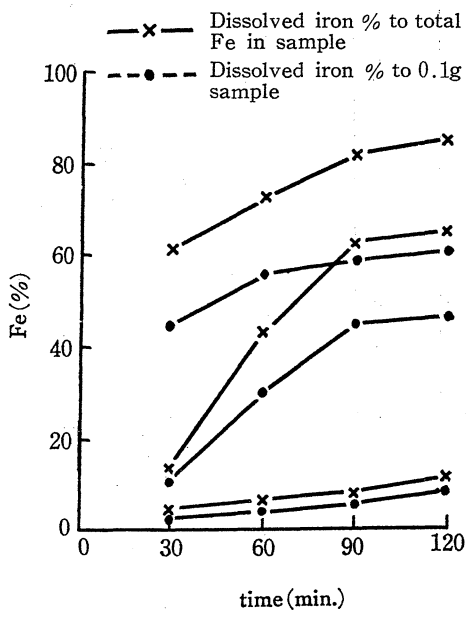


Fig. 2. Solubility of Fe in sandiron into 4 N-HCl sol.

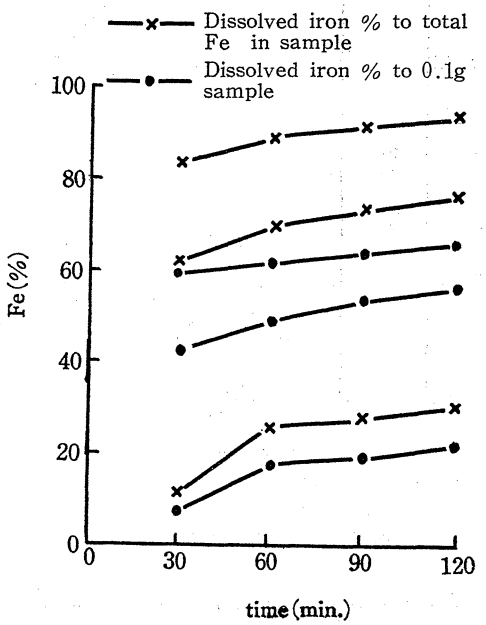


Fig. 3. Solubility of Fe in sandiron into 12 N-HCl sol.

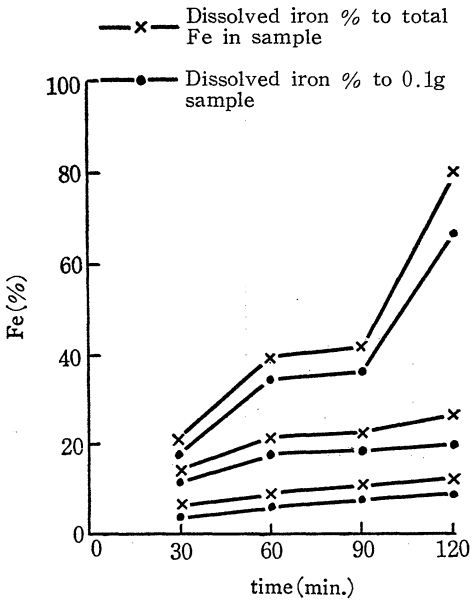


Fig. 4. Solubility of Fe in spongyiron into 4 N-HCl sol.

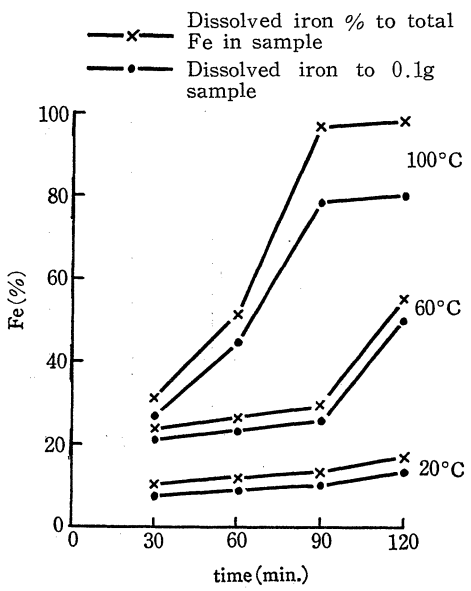


Fig. 5. Solubility of Fe in spongy-iron into 12 N-Hcl sol.

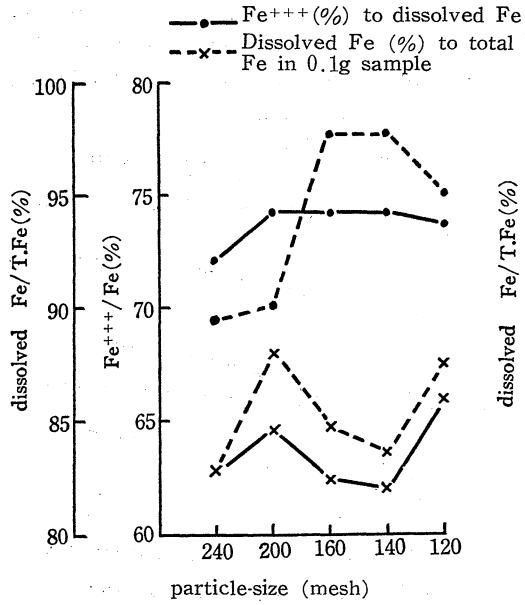


Fig. 6. Charasteristic solubility of Fe in sand-iron into 12 N-HCl sol. by particle-size at 20°C.

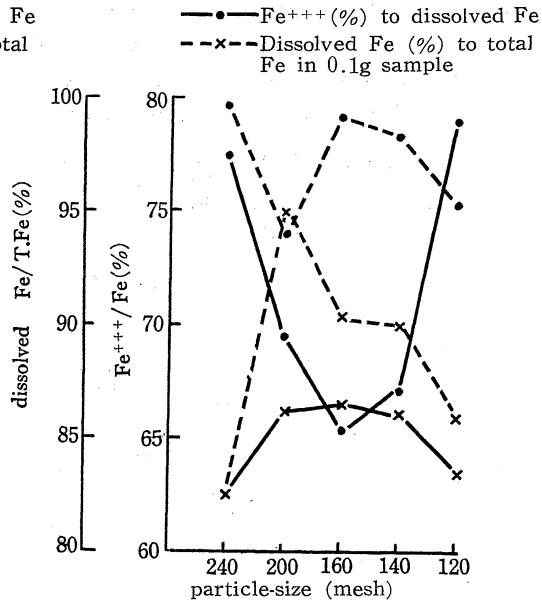


Fig. 7. Charasteristic solubility of Fe in sand-iron into 12 N-HCl sol. by particle-size at 60°C.

The fig. 6 and Fig. 7 give the solubilities of sand-iron in HCL solution ; by their patticlesizes there are no appreciable effects of temperature and time on the solubilities of 200 mesh sample, but the 200 mesh sample allows the much increase of the dissolution

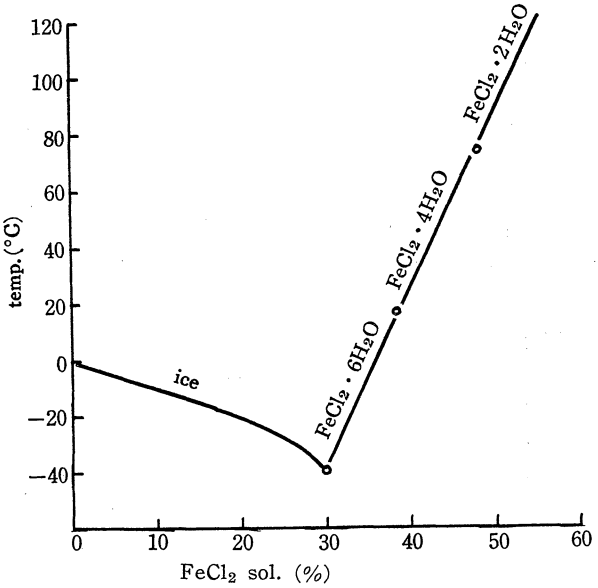


Fig. 8. Solubility curve of ferrous chloride.

of iron with the elevation of temperature and the elapse of time. It is not recognized that there is possible precise inclination of the increase of the concentration of $Fe^{+++}$ by the particle-sizes, but increase somewhat by the elaspe of time ; it is considered that the oxygen dissolved in the solution oxidises $Fe^{++}$ to $Fe^{+++}$. The solubility of ferrous chloride in water increases with t he elevation of temperature as in Fig. 8.[2)]

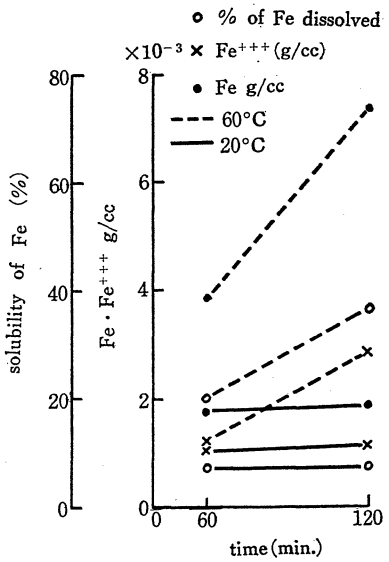


Fig. 9. Characteristric solubility of Fe in sand-iron into 12 N-$H_2SO_4$ sol. (Sample 0.02g/cc, 240~200 mesh)

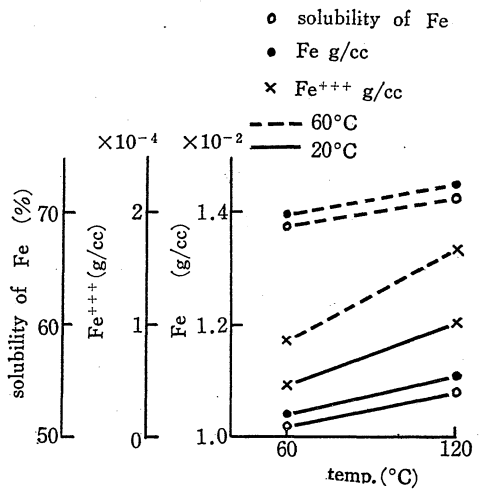


Fig. 10. Characteristic solubility of Fein spongy-iron into 12 N-$H_2SO_4$ sol. (sample 0.2g/cc, 240~200 mesh)

(B) Sulphuric acid

The Fig. 9 and Fig. 10. give the characterisric solubility curves of sand-iron and spongy-iron in 4N-$H_2SO_4$ solution.

Sand-iron dissolves in $H_2SO_4$ less than half in HCL, and the concentration of $Fe^{+++}$ is very low or zero. Spongy-iron dissolves easier into $H_2SO_4$ than sand-iron, but reverse into HCL, giving no $Fe^{+++}$ in both solutions. It is already known that the characteristic solubility of ferrous sulphate in water is in the fact that the maximum solubility of it is in the vicinity of 60°C on the solubility-temperature curve given in Fig. 2.[3)]

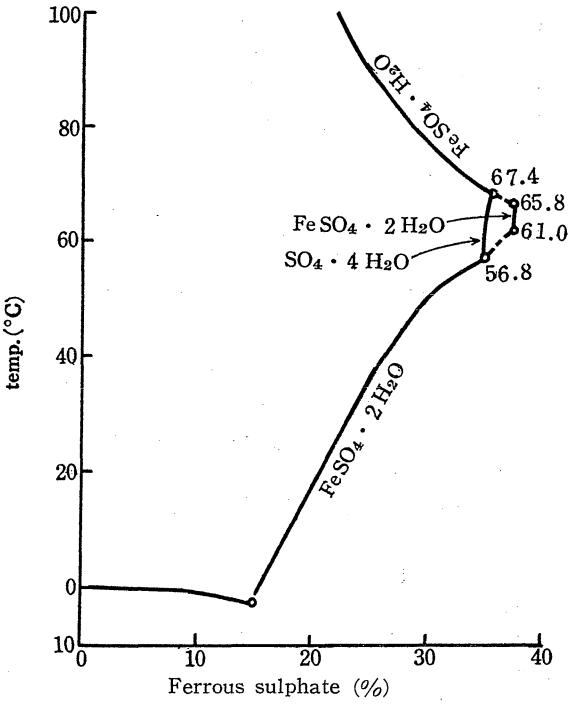


Fig. 11 Solubility curve oe ferrous sulphate in water

〔II〕 Air-oxydation of water solutions of iron salts.

(1) Ferrous Chloride

When each of the almost neutral solutions containing $Fe^{+++}$, obtained by dissolving sand-iron and spongy-iron inHCL respectively, which are controlled to be in the concentration of sample 0.1g/cc, is treated with air blow (1l/min.), the $Fe^{++}$ is oxydised slowly to $Fe^{+++}$ ; and the functional effect of the size of particles, temperature and time are indicated in Fig. 12—Fig. 14. In the cace of sand-iron, the particles of 140—240 mesh are markedly soluble and oxydizable compering with particles of the smaller and the larger mesh at 20°C for 60 min., and it is an interesting fact that for the 120—140 mesh particles, the $Fe^{+++}/Fe$ values measured befor and after air-blow at 20°C for 60 min., concentrate to the same point ; and it is undoubtedly concidered that in the case of 120—140 mesh particles ; under these experimental conditions, the rates of the

disolution of sand-iron in HCL and of the oxydation of $Fe^{++}$ to $Fe^{+++}$are parallel one another or the same. In the same series of experiments, if each particles of sand-iron is treated at 60°C, the dissolution and oxydation rates are extremly irregular with the exception of the fact that the concentration of those $Fe^{+++}/Fe$ values in the 120—140 mesh particles is similar to the case of 20°C.

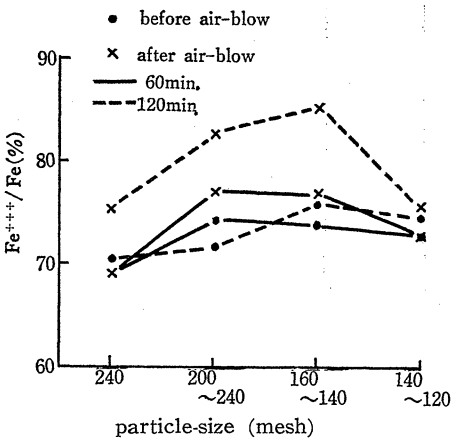


Fig. 12. Oxydation of HCl sol. of sand-iron by air-blow. (20°C, 1l air/min., 0.1g/cc)

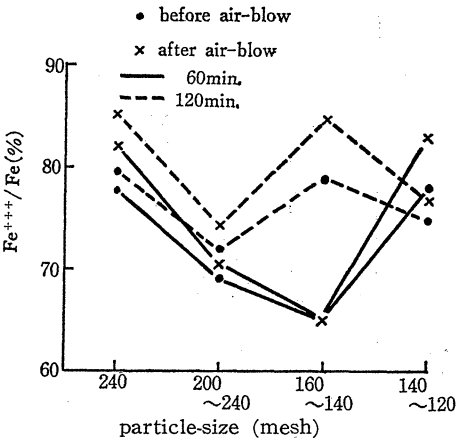


Fig. 13. Oxydation of HCl soln. of sand-iron by air-blow. (60°C, 1l air/min.)

In the cace of spongy-iron, the differences of particle-size and temperature affect regularly the rate of oxydation of $Fe^{++}$ to $Fe^{+++}$; the oxydation of rough particles proceeds rapidly, and that of fine ones very slowly.

The air-oxydation curve of the mixed solution of $FeCl_2$ and $FeCl_3$ in the hydrochloric acid solution is given in Fig. 15. Fig. 16.

The pure ($Fecl_2+Fecl_3$) solution and the pure $FeCl_2$ solution correspond to those of sand-iron and spongy-iron respectively. In the latter case, with the increase of the concentration of HCL, in spite of the slight absolute increase of $Fe^{+++}$, the $Fe^{+++}/Fe$ value somewhat elevate, but it falls in the former case.

From these results it can be known that the rate of oxydation of $Fe^{++}$ to $Fe^{+++}$ by air-blow is minus regulated with the higher concentration of the coexisting $Fe^{+++}$, and the higher the concentration of HCL elevate, the lower the $Fe^{+++}/Fe$ value becomes. Accordingly, it will be expected that, for instance, it must need much more time to oxydize $Fe^{++}$ to $Fe^{+++}$ for the formation of $\alpha$-FeO.OH or $\gamma$-Fe.OH in the wet method.

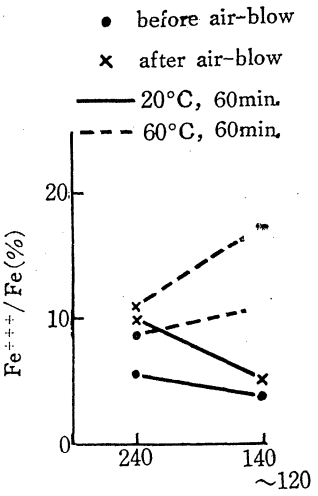


Fig. 14. Oxydation of HCl sol. of spongy iron by air-blow (0.1g/cc, 1l air/min.)

The oxydatiom ionpower of air-blow is calculated as follows ;

$$\frac{C_{Fe^{+++}}(\text{after air-blow}) - C_{Fe}(\text{before airb-low})}{\text{total Fe}} \times 100(\%)$$

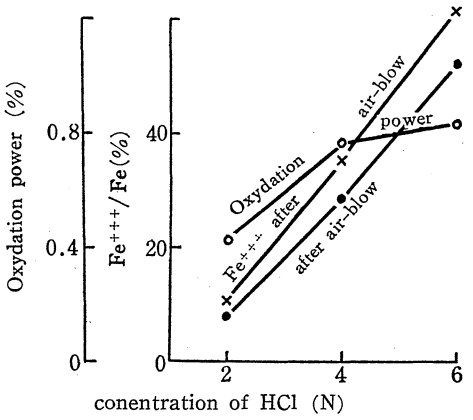


Fig. 15. Oxydation of HCl-$FeII_2$ sol. at 20°C (1l air/min., 2 mol. $FeCl_2$ sol. total volume 80cc.)

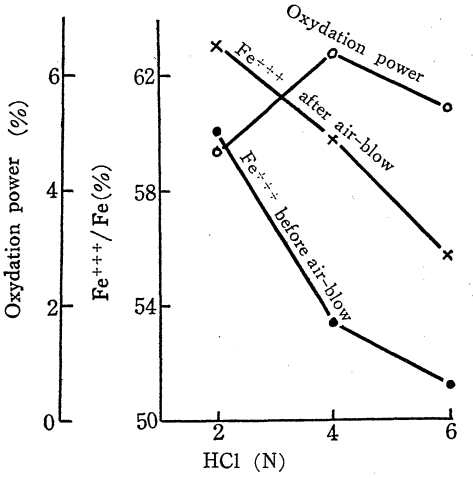


Fig. 16. Oxydation of ($FeCl_2$+$FeCl_3$) sol. by air-blow.
(1l air/min., 2 mol $FeCl_2$+2 mol $FeCl_3$, total volume 80cc.)

(2) Ferrous Sulphate

According to the above experiments, sand-iron and spongy-iron are treated with $H_2SO_4$ instead of HCl, as dissolving agents. (Fig. 17—Fig. 18) The particlesizes of samples are in 200—240 mesh. In the case of sand-iron, it is easely seen that the $Fe^{+++}/Fe$ values obtained before and after the air-oxydation at 20°C are very close, independent ot temperature, but the intervals of air-blow give a great effect on them. (Fig. 17)

On the contrary, the elevation of temperature from 20°C to 60°C lets the $Fe^{+++}/Fe$ value increase remarcablly (about 40%), indicating the oxydation rate of $Fe^{++}$ to $Fe^{+++}$ is to be rapidly promoted by air-blow and not the elaps of time.

In the case of spongy-iron, it offers quite different conditions as shown in Fig. 18, namely the great differences (40%—45%) are found between the values before and after air-blow, which are likely to be independent of the temperature and of the intervals of air-blow. (Fig. 18)

The air-blow effects in the solution of $FeSO_4 \cdot 7H_2O$ and the (1 mol. $FeSO_4$+0.39 mol. $Fe_2(SO_4)_3$) mixed solution are shown in Fig. 19 and Fig. 20.

As the ferrous solution contains no $Fe^{+++}$, the concentration of $Fe^{+++}$ titrated after air-blow mean the oxydation power for itself. The higher acid concentration elevates, the higher oxydation power become.

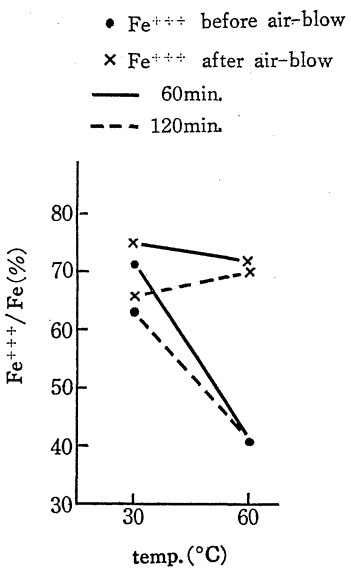


Fig. 17 Oxydation of Fe in $H_2SO_4$ acidic sol. of sand-iron by air-blow at 20°C. (11 air/min., 240~200mesh.)

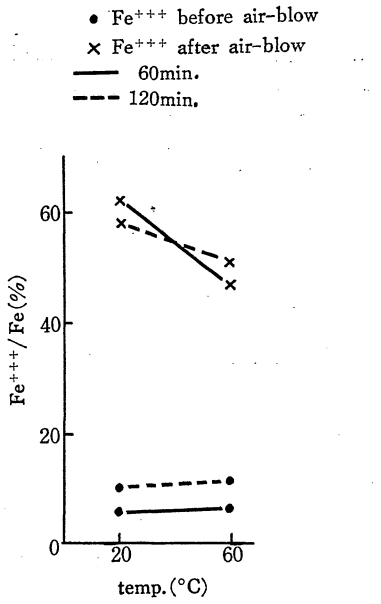


Fig. 18. Oxydation of Fe in $H_2SO_4$ acidic sol. of spongy-iron by air-blow at 20°C. (11 air/min., 240~200 mesh.)

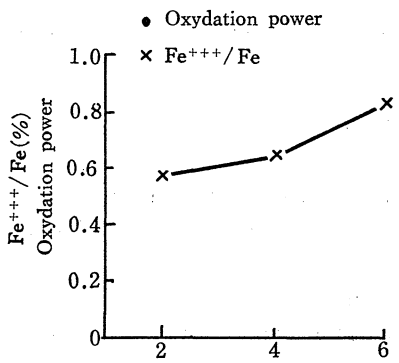


Fig. 19. Oxydation of $FeSO_4$ in $H_2SO_4$ acidic sol. by air-blow at 20°C. (1mol. $FeSO_4 \cdot 7H_2O$ sol., T. V. 60 cc, 11 air/min. )

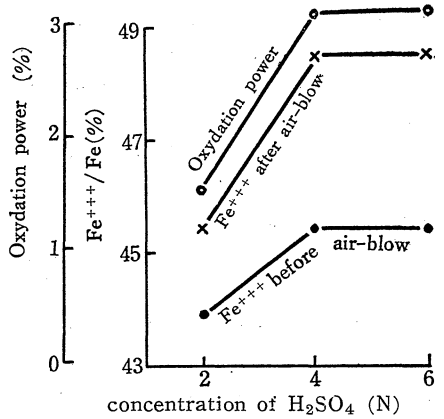


Fig. 20. Oxydation of Fe in $H_2SO_4$ acidic [$FeSO_4 + 0.39\ Fe_2(SO_4)_3$] sol. by airblow. at 20°C. (2 mol. $FeSO_4 \cdot 7H_2O + 1.8g\ Fe_2(SO_4)_3$: $Fe^{++}$ : $e^{+++} = 56.05 : 43.95 = 1 : 0.78$, T. V. 60cc, 11 air/min.

## Reterences

1) S. YAMAMOTO. "NIHONKAGAKUKAI-ZASSHI" **73**, 22–31 (1952).
S. YAMAMOTO. ibid., **74** 9–13 (1953).
2) T. INOUE. ; "RIKAGAKU-ZITEN", IWANAMI, (1953).
3) M. MORI, ; "KŌTŌ-KAGAKU-SHINRO N", vol., III, USHIDA-RŌKAKUHO (1944).