

A Study on the Recovery of Zn from Electric Arc Furnace Dust by Carbon Reduction

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There is a potential usability of electric arc furnace(EAF) dust produced during the iron manufacturing process as a recycled resource, because valuable materials such as Zn, Pb and Fe are contained in it. In this study, metallic Zn was recycled from the fine electric arc furnace dust by a solid state reduction method using carbon at relatively low temperature. It was possible to recover metallic zinc by using of high vapour pressure of zinc with this reduction method. The feasibility of recycled zinc for cold bonded pellet(CBP) was investigated. The main composition of EAF dust were franklinite($ZnFe_2O_4$), magnetite(Fe_3O_4) and zincite(ZnO), and Pb and Cl were completely removed by a heat treatment in oxidation environment. The reduction ratio increased as the solid carbon content increased, and it increased with decreasing of dust particle size and increasing of compaction pressure due to a increase of contact area.

Keywords : EAF dust, zinc, carbon, reduction, particle size, compaction pressure

1. Introduction

There is a potential usability of electric arc furnace (EAF) dust produced during the iron manufacturing process as a recycled resource, because valuable materials such as Zn, Pb and Fe are contained in it. It has been a obstacle to practically recover pure zinc from the dust due to impurities such as Pb, Cl and alkali where as the iron in the dust is effectively used for the raw material of blast furnace.

The EAF dust containing above stated impurities such as Pb and Cd can cause harmful effect for human body and environment, because toxic components are eluted with time in the case of simple abolition by conventional reclaim. Also, the micrometer or submicrometer dust particles can contaminate the air during open-air storage or transportation. Hence, the EAF dust was classified as harmfulness waste in 1980 by EPA of USA, after that it has been also regarded as harmfulness waste in Korea.

Recent trend of advanced countries to recycle zinc from EAF dust is not to simply abolish but to satisfy both economic and environmental aspect. For that, recycling of valuable materials as well as stabilization should be simultaneously satisfied, which is somewhat different concept compared to conventional simple abolition technology, then development of this technique is actively performed. Also, one of the most difficult problem to solve prior to recycle zinc is the complication of physical and chemical properties of dust. For example, high melting temperature, over 1,800°C of refractory materials such as dicalcium silicate($2CaO \cdot SiO_2$) and franklinite ($ZnO \cdot FeO_x$), re-dust by fine particle property in 10 ~ 100 μm range and low reactivity due to relatively low zinc content, compared to raw ore containing 40% of zinc.

Hence, lowering melting temperature, inhibiting re-dust and increasing reaction efficiency in low zinc concentration are key techniques, in order to economically recycle zinc from EAF dust.

In this study, systematic experiment was performed to recycle metallic zinc from EAF dust and carbon mixture by solid state reduction method using high zinc vapour pressure at relatively low temperature.

2. Experiment

Chemical compositions of EAF dust used in this study is presented in Table 1. The main phase contents are 59.4 wt.% of total Fe, 14.4wt.% of ZnO, 6.80wt.% of CaO and 3.5wt.% of Cl. The size distribution, mean particle size and specific surface area of EAF dust was varied from 1.0 to 100 μm , 3.94 μm and 1.5956m²/g respectively as shown in Fig. 1. And the density of EAF dust was from 1.1 to 2.3g/cm³. Also, the main compositions of EAF dust were Franklinite($ZnFe_2O_4$), Magnetite (Fe_3O_4) and Zincite(ZnO) from the result of XRD as shown in Fig. 2.

The dust particles, the size of which ranges from sub-micron to tens-micron, were mainly spherical like balls that were agglomerated each other from the result of SEM as shown in Fig. 3.

Fig. 4 shows the schematic diagram of experimental apparatus used for recycling zinc from EAF dust by reduction of carbon. Alumina tube with 65mm of diameter is located in the horizontal tube furnace, and the temperature is controlled by PID type of automatic temperature controller.

Firstly, pellets with 20mm of diameter was located in the furnace and temperature was increased and thus produced

fume dust from EAF dust was cooled down in chiller then collected by the dust collector.

The carbon used in the reduction reaction of EAF dust was charcoal of -325 mesh. The reduction temperature was ranged from 800 to 1,300°C with step of 100°C and the reduction time was set to 30, 60, 90 and 120min. The carbon contents was 5, 10, 15, 20, 25 and 30wt.% and the dust was classified by wet sieving with +100, -100/+140, -140/+200, -200/+270, -270/+325 and -325mesh. And, the compaction pressure was varied from 500 to 1500psi.

The chemical compositions was analyzed by X-ray fluorescence analyzer(XRF) and chemical titration analysis, and the phase of dust was investigated by X-ray diffractometer(XRD). The thermal properties such as reduction reaction and weight changes and microstructures were studied by simultaneous thermal analyzer and scanning electron microscopy(SEM) respectively.

Table 1. The chemical compositions of EAF dust used in this study(wt.%).

Elements	Contents	Elements	Contents
T, Fe	59.4	Na ₂ O	0.36
ZnO	14.4	K ₂ O	1.40
CaO	6.80	P ₂ O ₅	0.34
MgO	2.92	C	1.30
MnO	2.48	S	0.40
SiO ₂	1.85	Pb	0.001
Al ₂ O ₃	0.39	Cl	3.50
TiO ₂	0.05	Cd	Tr

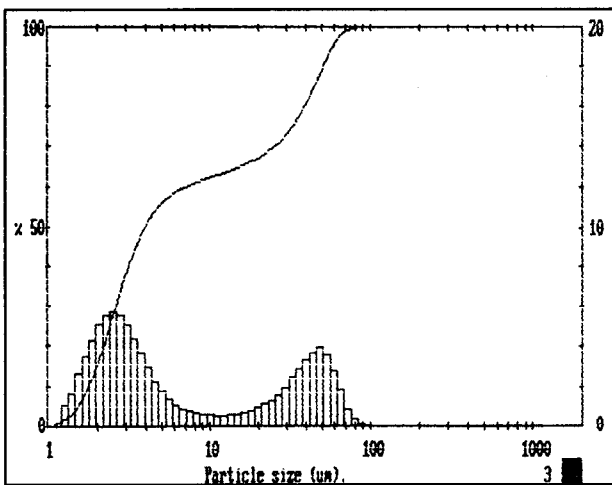


Fig. 1. Particle size distribution of EAF dust used in this study.

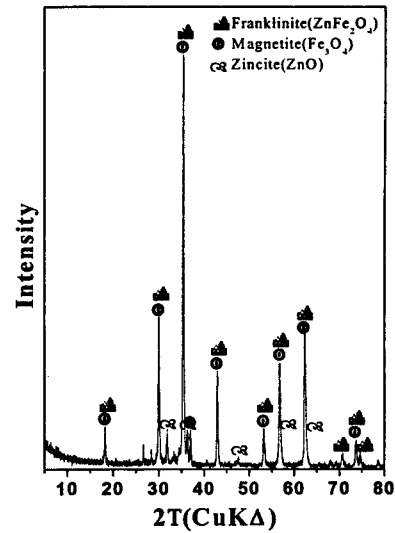


Fig. 2. X-ray diffraction pattern of EAF dust used in this study.

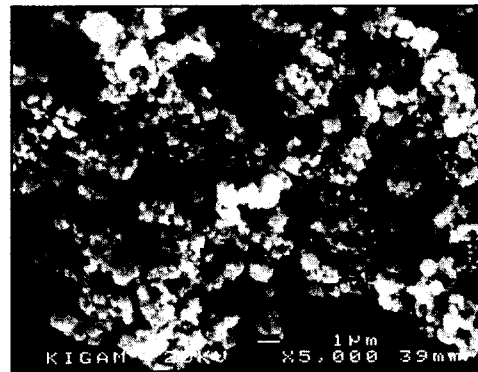


Fig. 3. Scanning electron micrograph of EAF dust used in this study.

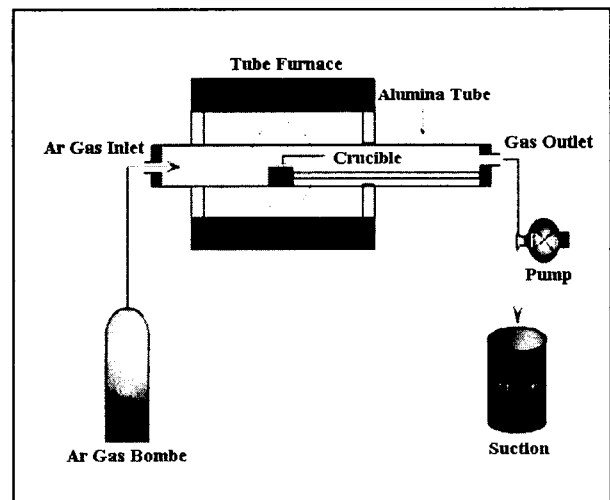


Fig. 4. The schematic diagram of experimental apparatus.

3. Results and Discussion

Fig. 5 shows TG-DSC curve of EAF dust by the reaction of carbon. There were an endothermic and a weight loss at 150 °C by the decomposition of combined water. It is expected that the 1st reduction such as $ZnFe_xO_y(s) + yC(s) = ZnO(s) + Fe_xO_y(s) + yCO(g) + yCO_2(g)$ and $ZnO(s) + CO(g) = Zn(g) + CO_2(g)$ takes place at around 718 °C. Also, the weight loss at 932 °C is attributed to the volatilization by the reduction of Fe_3O_4 and ZnO by carbon. That is, 2nd reduction reaction such as $ZnO(s) + C(s) = Zn(g) + CO(g)$, $Fe_xO_y(s) + yCO(g) = xFe(s) + yCO_2(g)$ and $CO_2(g) + C(s) = 2CO(g)$ so called Boudouard reaction could take place at around 932 °C.

Hence, the reduction reaction of the dust by carbon is governed by the 2nd reduction at 932 °C rather than the 1st reduction at 718 °C.

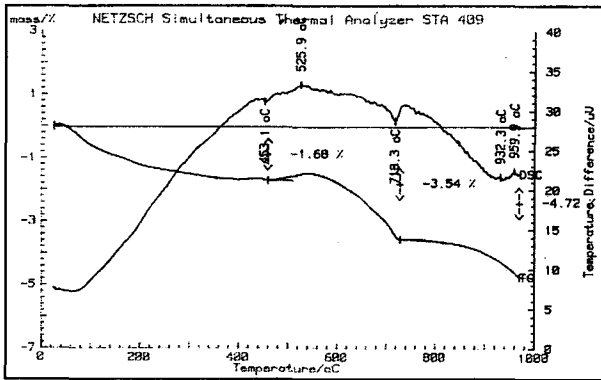


Fig. 5. TG-DSC curve of electric arc furnace dust used in this study.

Fig. 6 and Table 2 show the possible main reaction in the EAF dust and carbon mixture and Gibbs free energy change (ΔG°) respectively. It is found that the standard Gibbs free energy is linearly changed according to temperature. Among the reactions, the standard Gibbs free energy of $ZnO(s) + C(s) = Zn(g) + CO(g)$ changes to negative at 950 °C and the Gibbs free energy of $ZnFe_2O_4(s) + 2C(s) = Zn(g) + 2FeO(s) + 2CO(g)$ significantly decreases as the temperature increases, hence these reduction reactions are expected to be took place over 950 °C and 736 °C respectively.

Fig. 7 shows the reduction model of pelletized dust by carbon applied in this study. It has been reported that the reduction reaction takes place along the radial direction of a pellet by solid carbon over 800 °C. Also, the reduction reaction takes place toward outside of the pellet through pores or surface by diffusion of the evolved gas phase carbon. From Fig. 6, the reaction, $CO_2(g) + C(s) = 2CO(g)$ finishes below 850 °C, whereas the reactions such as $ZnO(s) + CO(g) = Zn(g) + CO_2(g)$ and $FeO(s) + CO(g) = Fe(s) + CO_2(g)$ are continuously reduced over 850 °C.

However, there is some temperature deviation in the

proposed mechanism compared to the TG-DSC result which expect 1st and 2nd reduction reaction at 718 and 932 °C respectively in Fig 5, but overall mechanism seems to be well agreed to the reported pellet reduction mechanism.

Fig. 8 shows the X-ray diffraction pattern of wet meshed EAF dust by +100, -100/+140, -140/+200, -200/+270, -270/+325 and -325mesh respectively. In the case of as received EAF dust, $ZnFe_2O_4$ is main phase even though Fe_3O_4 and ZnO are presented. As the particle size decreased, the ZnO and SiO_2 phase increased but $ZnFe_2O_4$ and Fe_3O_4 phase of spinel structure decreased. Hence it was confirmed that the composition of EAF dust quantitatively varies with particle size, even though the components are same.

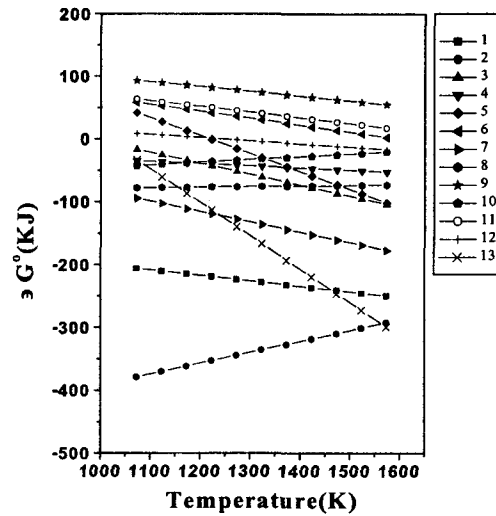


Fig. 6. Standard Gibbs free energy (ΔG°) of each reaction in EAF dust with temperature.

Table 2. Standard Gibbs free energy (ΔG°) of each presumption reaction in EAF dust.

Presumption Reaction	ΔG°	No
$C(s) + 1/2O_2 = CO(g)$	$-111960 - 87.78T$	1
$2CO(g) + O_2(g) = 2CO_2(g)$	$-564840 + 173.3T$	2
$C(s) + CO_2(g) = 2CO(g)$	$170460 - 174.43T$	3
$Fe_2O_3(s) + CO(g) = 2FeO(s) + CO_2(g)$	$2515 - 34.93T$	4
$ZnO(s) + C(s) = Zn(g) + CO(g)$	$348480 - 286.1T$	5
$ZnO(s) + CO(g) = Zn(g) + CO_2(g)$	$178020 - 111.67T$	6
$PbO(l) + C(s) = Pb(m) + CO(g)$	$83140 - 165.48T$	7
$PbO(l) + CO(g) = Pb(m) + CO_2(g)$	$-87320 + 8.95T$	8
$ZnO(s) + 2FeO(s) = Zn(g) + Fe_2O_3(s)$	$175505 - 76.74T$	9
$PbO(l) + 2FeO(s) = Pb(m) + Fe_2O_3(s)$	$-89835 + 43.88T$	10
$ZnO(s) + 3FeO(s) = Zn(g) + Fe_3O_4(s)$	$162854 - 92.48T$	11
$PbO(l) + 3FeO(s) = Pb(m) + Fe_3O_4(s)$	$62790 - 50.65T$	12
$ZnFe_2O_4(s) + 2C(s) = Zn(g) + 2FeO(s) + 2CO(g)$	$536090 - 530.9T$	13

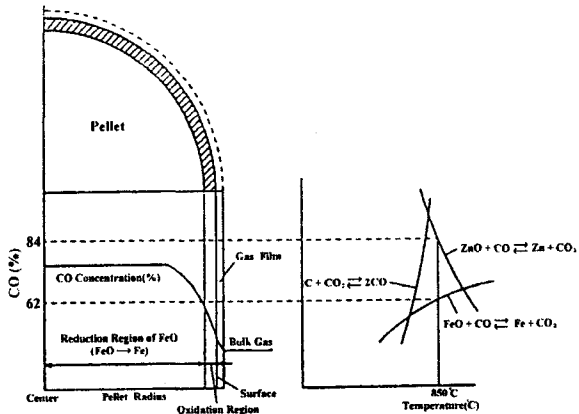


Fig. 7. Pellet reduction model of EAF dust by carbon.

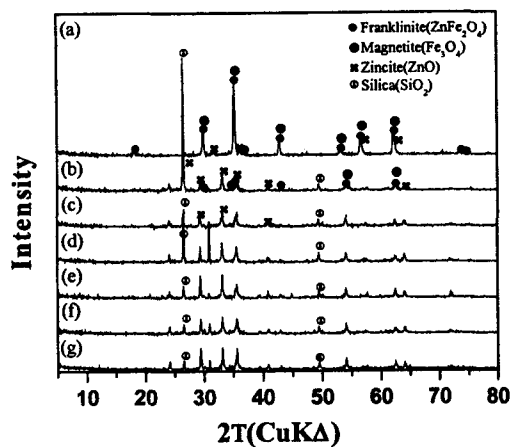


Fig. 8. X-ray diffraction patterns of EAF dust with particle size ; (a)Not Seiving, (b)+100, (c)-100/+140, (d) -140/+200, (e)-200/+270, (f)-270/+325 and (g) -325mesh.

In order to remove Pb and Cl prior to reduce by carbon, the pellets compacted with 1500psi were heat treated in oxidative atmosphere as functions of reaction temperature and particle size for 1 hr. Fig. 9 shows the result for the variation of volatilization rate of Fe, Zn, Pb and Cl. There was any significant change in the volatilization rate of Fe and Zn from Fig. 9. However 80% of Pb was volatilized over 1000°C where as it shows low volatilization rate under 1000°C. In the case of Cl, the volatilization rate was 50~60% under 1000°C, but it drastically increased over 1000°C and reached to nearly 100%. Also, the volatilization rate of Pb and Cl increased as the particle size decreased, because contact area increased as the particle size decreased then the volatilization rate of Pb and Cl slightly increased.

Fig. 10 shows the result of volatilization rates of zinc in EAF dust by carbon contents and reduction temperature for 1hr in Ar atmosphere. In the case of without reducing

agent, the volatilization rate of zinc slightly increased as the reduction temperature increased due to the minute carbon content(1.3wt.%) in the EAF dust. And it was ranged from 10 to 50% at the temperature of 800 and 900°C. When the carbon content was 30wt.%, the volatilization rate of zinc were 80% at 1000°C of reaction temperature. And the volatilization rate of zinc were 98, 99 and 99% respectively at 1100, 1200 and 1300°C. Also, the volatilization rates of zinc slightly increased as the particle size decreased as shown in Fig. 11.

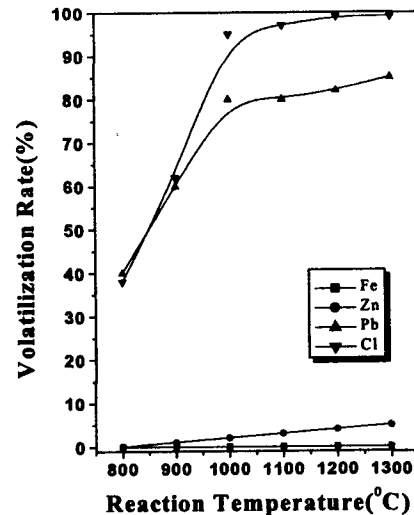


Fig. 9. The volatilization rates of Fe, Zn, Pb and Cl in oxidation atmosphere with temperature.

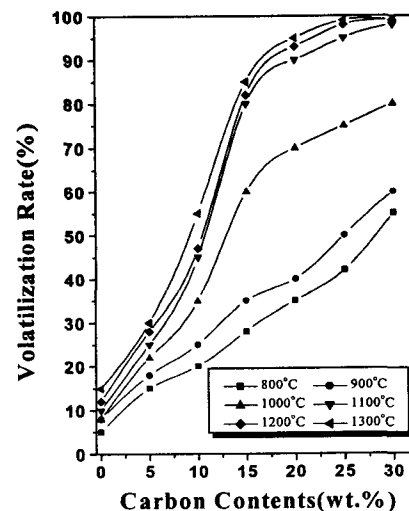


Fig. 10. The volatilization rates of zinc with carbon contents and reduction temperature for 1hr Ar atmosphere.

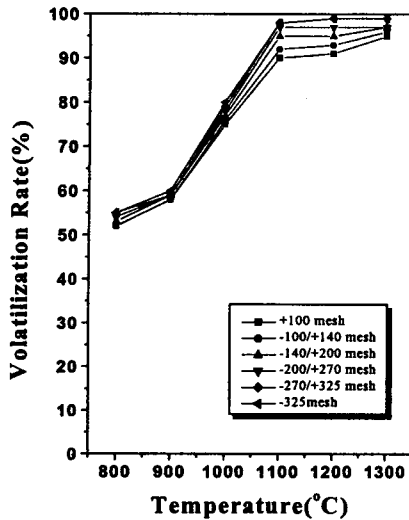


Fig. 11. The volatilization rates of zinc with particle size and reduction temperature of EAF dust.

Fig. 12 shows the result of volatilization rates of zinc in EAF dust by reduction temperature and time in Ar atmosphere. And the carbon content was 30wt%. The volatilization rate of zinc slightly increased as the reaction temperature increased and the reduction fraction of zinc linearly increased. At 1000°C of reduction temperature, the volatilization rates were 78% until 60 min and 97% for 120 min. And volatilization rates were 87%, 97%, 98% and 99% for 30, 60, 90 and 120 min respectively at 1100°C. Finally, it was 99% for 30min at 1200°C and showed nearly 100% over 60 min.

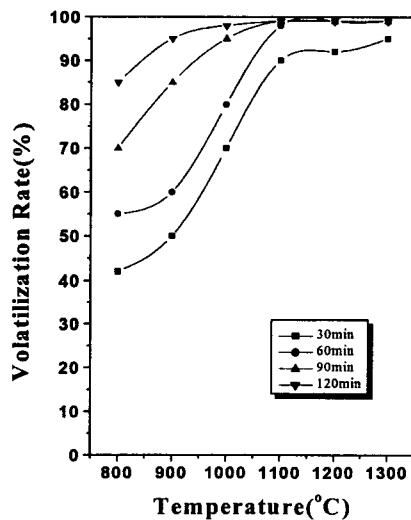


Fig. 12. Results of volatilization rates of Zn with reduction temperature and time in Ar atmosphere.

Fig. 13 shows the volatilization rates of zinc by compacting pressure and reduction temperature in 1hr at Ar atmosphere, where the contents of solid carbon were 30wt%. It was confirmed that the volatilization rate of Zn gently increased as the compacting pressure increased due to the increases of reactivity between carbon and EAF dust by the contact area increases.

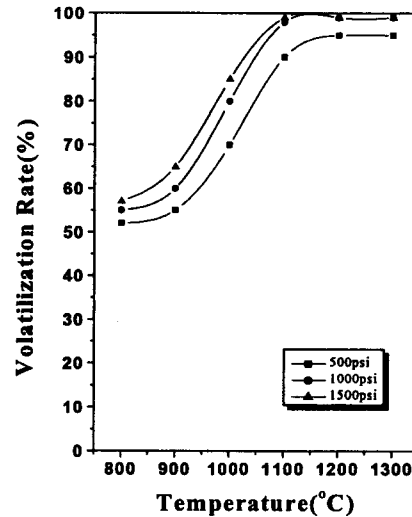


Fig. 13. Results of volatilization rate of zinc with compacting pressure and reduction temperature in 1hr at Ar atmosphere.

4. Conclusion

A study on the recycling of zinc by the reduction of EAF dust was conducted, and the effects of particle size, reduction temperature, time and compacting pressure are summarized as followings;

1. The main compositions of EAF dust were $ZnFe_2O_4$, Fe_3O_4 and ZnO , and ZnO and SiO_2 phase increased as the particle size decreased. It was shown that the 1st and 2nd reduction reaction took place at 718 and 932°C respectively from TG-DSC result.
2. The volatilization rates of Fe and Zn, Pb and Cl slightly increased as the reduction temperature.
3. When the carbon content was 30wt.%, the volatilization rate was ranged from 10 to 50% at the temperature of 800 and 900°C and it was 80% at 1000°C. And the volatilization rate of zinc were 98, 99 and 99% respectively at 1100, 1200 and 1300°C. Also, the volatilization rate of zinc slightly increased as the particle size decreased
4. The volatilization rate of zinc slightly increased as the reaction temperature increased and the reduction fraction of zinc linearly increased. At 1000°C of

reduction temperature, the volatilization rate were 78% until 60 min and 97% for 120 min. And it was 87%, 97%, 98% and 99% for 30, 60, 90 and 120min respectively at 1100°C. Finally, it was 99% for 30min at 1200°C and showed nearly 100% over 60 min.

5. The volatilization rate of zinc by compacting pressure and reduction temperature in 1hr at Ar atmosphere, where the contents of solid carbon were 30wt%. It was confirmed that the volatilization rate of zinc gently increased as the compacting pressure increased due to the increases of reactivity between carbon and EAF dust by the contact area increases.

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