The Micro-Changes of Fly Ash in the Utilization of “Dip in One Acid Twice/Unite Two Kinds of Alkalis”

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The Micro-Changes of Fly Ash in the Utilization of “Dip in One Acid Twice/Unite Two Kinds of Alkalis”

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Determined the new technology of element leaching in fly ash’s utilization---- “dip in one acid twice/unite two kinds of alkalis” through comparison tests, the technique consist of four phases: acid leaching、alkali dissolution, calcination and second acid leaching, the maximum fine utilization rates of silicon, aluminum, iron are respectively 97.07%, 86.67%, 96.54%, the total utilization rate is 100%. Analyzed the micro-changes of fly ash in the utilization process by X-ray diffraction and scanning electron microscope, the results show that: (1)there are mineral changes exist in acid leaching process, and some amorphous active substance is dissolved, it destroy the surface structure of fly ash, conducive to the conduct of following response; (2)after alkali leaching, most of the amorphous SiO_2 is dissolved, crystalline SiO_2 (quartz) has not changed; (3)after calcination with sodium carbonate, all the mine phases are transformed into nepheline and a small amount of pyroxene which are layer (film) structure , except a small amount of residual quartz crystal;(4)after the second acid leaching, the fly ash is transformed into silica II which mainly constitute by the amorphous SiO_2.

Keywords : Fly ash, X-ray diffraction, Scanning electron microscopy

1 INTRODUCTION

At present, fly ash was mainly applied to the construction [1,2], building materials, transport and soil improvement, etc., only a small number of fly ash was applied to the environmental protection[3] and chemical industry[4,5]. Although construction and transportation need a large quantity of fly ash and improve the utilization rate of fly ash in short time, these were all low value-added product, the fly ash potential value was not taken use of and economic benefit was low, therefore, developing high value-added products of fly ash was the main technology research directions of fly ash resource recycling. In this paper, we introduced the utilization of fly ash in environmental protection and chemical engineering, improved the traditional acid-leaching and alkali dissolution method by using exploratory experiment, at last determined the new technology of element leaching in fly ash’s utilization--the technique of “dip in one acid twice/unite two kinds of alkalis” method. The main components (silica, alumina and iron oxide) of fly ash was basically all used with this method, no waste residue and waste liquid, obtained the harmony of economic, social, and environmental effectiveness.

2 EXPERIMENT MATERIALS AND METHODS

2．1 Experiment materials

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In this experiment, the raw materials of fly ash was obtained from the second phase of power plants of Pingdingshan Coal Industry Group, the chemical composition shown in Table 1, other raw materials such as hydrochloric acid, sodium hydroxide, soda ash are all analytically pure and chemically pure.

2．2 Determination method

In this experiment, the determination methods of the main indicators are shown in Table 2.

2．3 Experiment Method

Based on the previous experiment, we design four plans:

Plan one: Mixed fly ash with sodium carbonate acid leaching after roasting. After drying, weighed fly 10g of fly ash is mixed with 10g sodium carbonate, then it is lapped and placed in muffle furnace in 900 degrees Celsius heat preservation 2 hour. After natural cooling, it is added one to one hydrochloric acid in 80 degrees Celsius heat and dissolution, and lifts down and agitates with water, then it is filtered. Constant volume filtrate at 250ml, is measured, and the concentration of silicon, aluminum and iron in filtrate , at last calculated their contents.

Plan two: Mix acid leaching fly ash with not acid leaching sodium carbonate to roast, then do second time acid leaching. Weigh drying fly ash 10g, then do acid leaching according to confirmed acid leaching parameter of orthogonal experiments, filter, according to one to one mixed dregs with sodium carbonate, following is the same as Plan one.

Plan three: Mix alkali leaching fly ash with not alkali leaching sodium carbonate to roast, then do acid leaching. Weigh drying fly ash 10g, then do dissolution for 2 hour with 25 percent concentration of sodium hydroxide under the conditions of 100 degrees Celsius heat, filter, according to one to one mixed dregs with sodium carbonate, following is the same as Plan one.

Plan Four: Mix alkali leaching and do acid leaching fly ash with sodium carbonate to roast, then do second time acid leaching. Weigh drying fly ash 10g, then do acid leaching according to confirmed acid leaching parameter of orthogonal experiments, filter, then do dissolution for 2 hour with 25 percent concentration of sodium hydroxide under the conditions of 100 degrees Celsius heat, second time filter, according to one to one mixed dregs with sodium carbonate, following is the same as Plan one.

3 RESULTS AND DISCUSSION

3．1 The determination of Technology program

According to the use of intermediate products derived from experiment, the results of four kinds of programs’ data processing are obtained (see Table 3).

As can be seen in Table 3, for the preparation of PAFC, the highest leaching rate of aluminum and iron is program 4 in the four kinds of programs (Al leaching

Table 1. The chemical composition of fly ash

Project	silicon dioxide	aluminum oxide	ferric oxide	titanium dioxide	calcium oxide	magnesia	sodium oxide	kalia	Loss
Contents (%)	54.65	29.12	5.98	0.76	4.31	1.26	0.42	1.10	2.4

Table 2. The determination method of experiment

Analysis Project	determination method	primary instrument
Fe^{3+} and Al^{3+}	fluoride to replace the EDTA titering process	electric stove, buret
SiO_2	eeduction of silicon molybdate	722 spectrophotometer
mineral constituent	X- diffraction analysis	D8ADVANCE X-diffraction analysis analyzer
micromechanism	scanning electron microscope analysis	JSM-6390LV scanning electron microscope

Table 3. The analysis of Si, Al, Fe of four improved programs

Use	PAFC			Silica I			Silica II		
Source	Solution A+ Solution C			Solution B			Residue C		
Index	Al (%)	Fe (%)	Si (%)	Al (%)	Fe (%)	Si (%)	Al (%)	Fe (%)	Si (%)
Scheme 1	74.07	88.06	4.43	——	——	——	22.86	8.65	92.79
Scheme 2	67.81	92.13	8.35	——	——	——	28.66	6.57	89.25
Scheme 3	59.96	90.35	5.20	2.35	3.45	6.52	34.43	3.5	85.37
Scheme 4	86.67	96.54	1.67	4.32	2.84	43.22	1.02	1.25	53.85

Note:
Solution A—the solution after acid leaching;
Solution B—the solution after alkali dissolution;
Solution C—the acid leaching solution of residue B calcinate with sodium carbonate;
Residue C—the acid leaching residue of residue B calcinate with sodium carbonate.

rate is 86.67%, iron leaching rate is 96.54%). Moreover, silicon content in the solution produced by preparation of PAFC in program 4 (solution A + solution C) is the lowest, only 1.67%, and will not affect polymerization of aluminum and iron, so program 4 is the best option. For the preparation of silica, Al-Fe content of residue C in program 1, 2 and 3 is too high, which can not obtain silica products directly. In contrast, Al-Fe content is less in program 4, and silica II can be obtained from residue C through drying, besides, the silicon leaching rate is 43.22% in the alkali-soluble process, a higher quality silica I can be obtained, the utilization of SiO_2 in the preparation of silica is as high as 97.07%, so program 4 is the best program.

By the exploration of above-mentioned four kinds of improvement programs, program 4 is the best option. Based on program 4, the overall program flow is designed as shown in Fig. 1.

The technology program has two major characteristics: (1) Fly ash is fully used, namely utilization rate is 90%, and the remaining 10% is used as building material additives; (2) Fly ash is used as chemical raw materials recycling in various process, which obtain not only cost saving but energy efficiency and emission reduction, which is in line with clean production requirements.

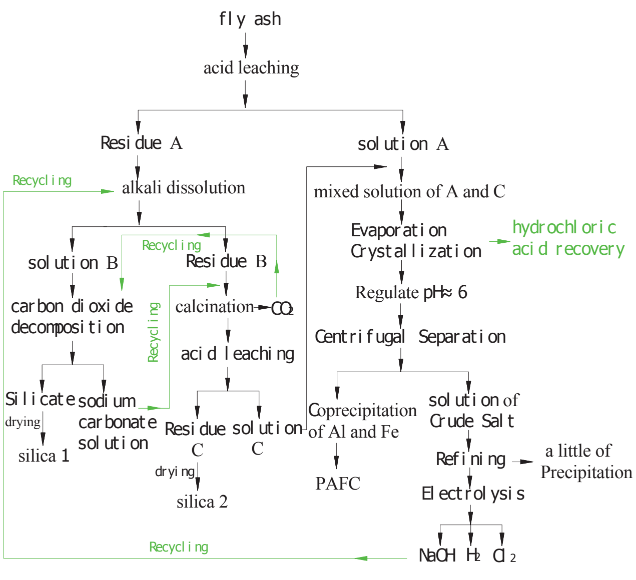

Fig. 1. The overall use technology of Fly Ash

3．2　The micro-change analysis of fly ash in the use of process

In the whole utilize project the fly ash experience four phases: acid pickling, alkaline leaching, adding sodium carbonate to help dissolve and the second acid pickling. Before and after the four phases, there are five states of existence for fly ash, Respectively the original fly ash (records primitive ash), the ash dregs after acid pickling(records dregs A), the ash dregs after alkaline leaching (records dregs B), the clinkering of after adding the sodium carbonate roasting (records roasting clinkering),the ash dregs of after second acid pickling(records silica II). Through contrast the X-diffraction patterns and scanning electron microscope image of five states for fly ash, from the mineral composition and micro-structural analysis the change process of fly ash in these technical programs.

(1) Primitive ash

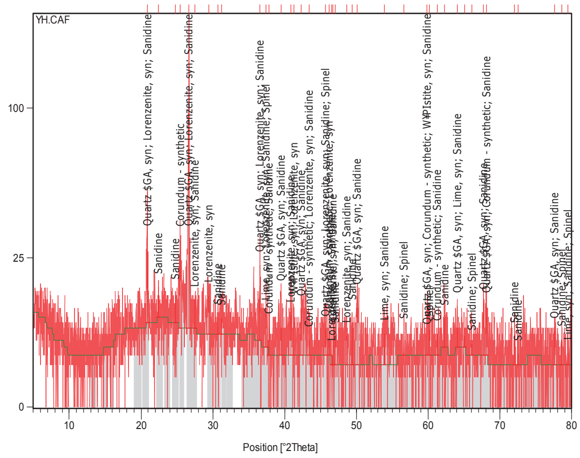

Fig. 2. X-diffraction patterns of primitive ash

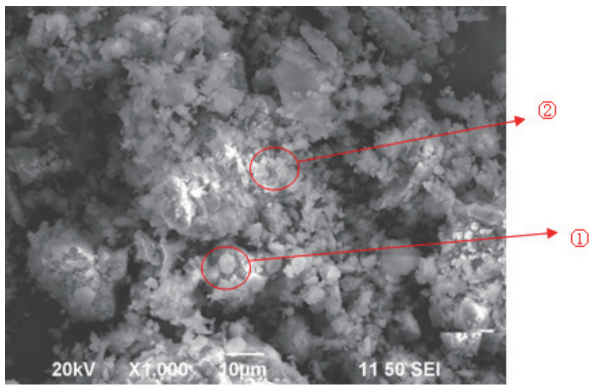

Fig. 3. SEM chart of primitive ash

From X-diffraction patterns of primitive ash, it can be seen that they have a clear hill-like peak and diffuse peak, therefore, the primitive ash contains more amorphous material and amorphous vitreous, also through an analysis of the characteristic peaks can tell that of primitive ash crystalline mineral are quartz, mullite, magnetite, anhydrite, hematite, glassy feldspar, lorenzenite and spinelle.

By the scanning electron microscope image can be seen the primitive ash are sharply divided on the shape and size, some of particle surface smooth(as ①)but some rough(as ②), gather together form a collection particles with large angular. From the micro-structure, this is became that the fly ash contains more amorphous material and amorphous vitreous and this is consistent with X-diffraction analysis. These vitreous bodies assume micro beaded, sponginess and so on anomalous shape, even if some crystal also assumes the non-regular shape, as mullite is the small acicular crystal adhere to the vitreous body surface, or by vitreous body package; From the forming process, this is because ash particles into the furnace combustion chemical composition, shape, particle size are different, the degree of combustion in the furnace and the discharge means also have differences, therefore, the formation of fly ash particle composition are also very unstable.

(2) Dreg A

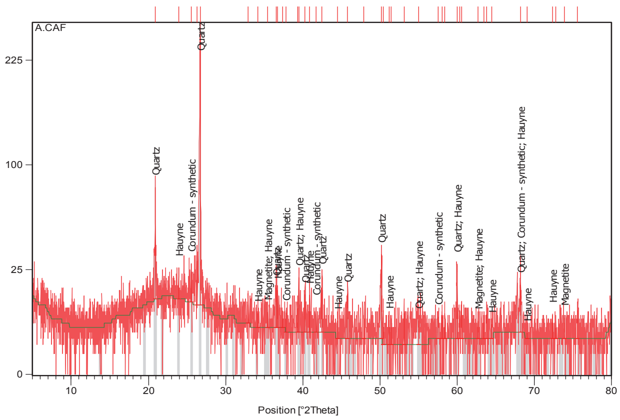

Fig. 4. X-diffraction patterns of dreg A

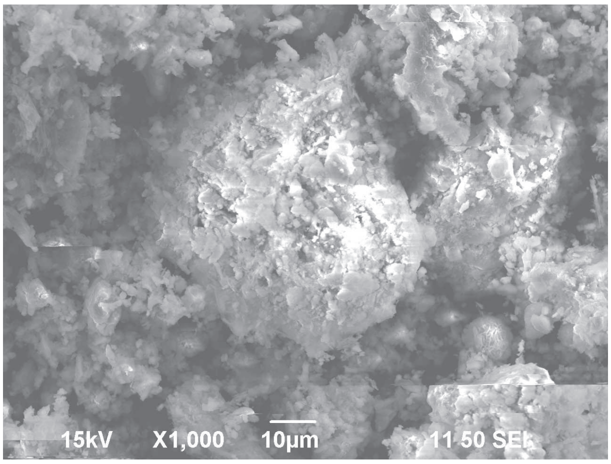

Fig. 5. SEM chart of dreg A

From the X-diffraction of residue A, it can be seen that there was a marked hill-like peak and dispersion peak. So the same residue A and the original ash contains more amorphous material, and the analysis of characteristic peaks revealed that the crystalline minerals of residue A are quartz, mullite, magnetite and blue square stone. Compared to crystalline minerals of the original ash, those can be drawn: In the acid leaching process, three crystalline mineral phases(quartz, mullite, and magnetite)has not changed, which indicates that they are insoluble, or insoluble for the acid, and their mineral phase can not be dissolved or changed using acid leaching. For hematite, anhydrous gypsum, transparent feldspar, silicon and sodium titanium spinel, the role of acid leaching is still relatively large, that hematite can be completely dissolved or partially dissolved into magnetite phase, that part of anhydrous gypsum, transparent feldspar, silica sodium perovskite and spinel can be partially dissolved into a blue square stone mineral phase. Some active materials of amorphous mineral phase react with the HCl (chemical equation see type 1). This series of reactions can greatly undermine the structure of the surface of fly ash particles, and increase its surface areas, which are conducive to the follow-up reaction.

$$Al_2O_3+6HCl \longrightarrow 2AlCl_3+3H_2O$$
$$Fe_2O_3+6HCl \longrightarrow 2FeCl_3+3H_2O$$
$$CaO+2HCl \longrightarrow CaCl_2+H_2O \qquad \text{(Formula 1)}$$
$$MgO+2HCl \longrightarrow MgCl_2+H_2O$$
$$Na_2O+2HCl \longrightarrow 2NaCl+H_2O$$

As can be seen from Fig. 5, after acid leaching, some small particles in the fly ash are dissolved by acid (dissolved constituents and response equation, see Equation 1), large and small particles surface that has not been dissolved are subject to a certain corrosive effect, which lay the foundation for the next step alkali-soluble.

(3) Dreg B

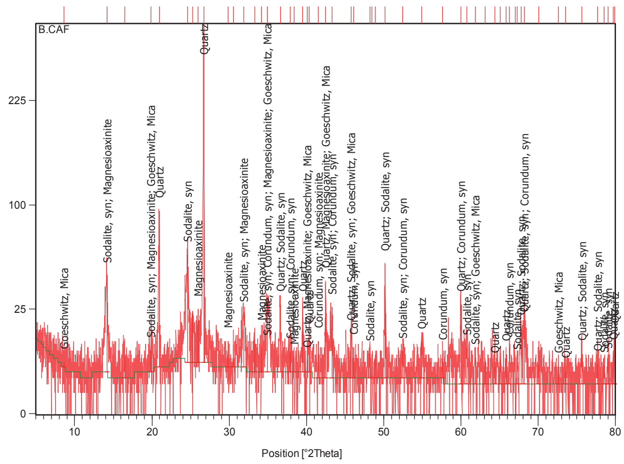

Fig. 6. X-diffraction patterns of dreg B

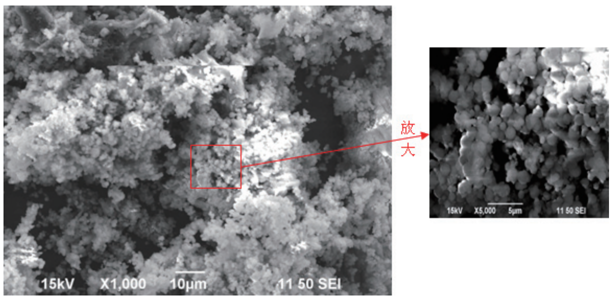

Fig. 7. SEM chart of dreg B

By the analysis of characteristic peaks of Slag B-diffraction pattern, it can be shown that the crystallize minerals phase in slag B are mainly quartz, sodalite, illite. And compared to their crystallized phase in slag A, those can be known: After alkali dissolution, the amorphous SiO_2 is completely dissolved, while the mineral phase of crystalline SiO_2 (quartz) has not changed. Blue square stone, glassy state of alumina and magnetite are changed into sodalite and illite under the conditions of alkali dissolution. The main chemical reaction formula: $SiO_2+2NaOH \rightarrow Na_2SiO_3+H_2O$.

As can be seen in Fig. 7, after alkali dissolution, the micro-structure of ash has undergone great changes, appear as spherical particles of the similar size, shape and smooth surface bonds with each other, because in the process of alkali dissolution, amorphous SiO_2 and materials soluble in alkaline are almost completely dissolved. While the blue square stone, glass state of alumina, magnetite and others changed into sodalite and illite under the conditions of alkali dissolution, which structure is relatively regular mineral phase.

(4) Soda slag

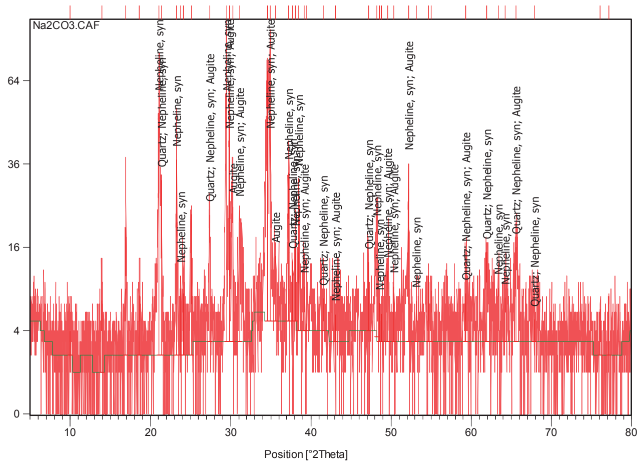

Fig. 8. X-diffraction patterns of Soda slag

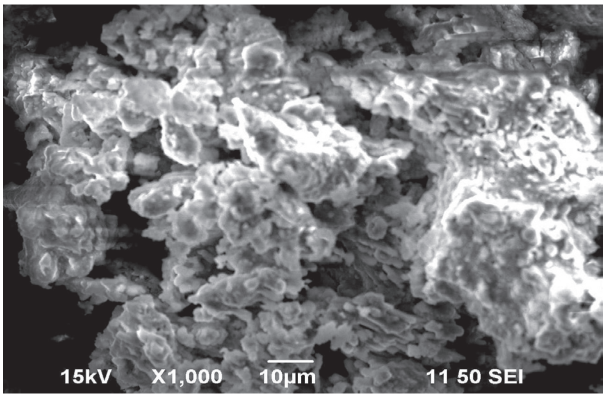

Fig. 9. SEM chart of Soda slag

By the analysis of characteristic peaks of sodium carbonate slag X-diffraction pattern, it can be known that crystallize minerals phase is quartz, nepheline and pyroxene after adding sodium carbonate and mixed roasting, which small amount of quartz and pyroxene, nepheline dissolve in acid easily. Thus, after second acid leaching, silicic acid is obtained mixed with a small amount of impurities, and dried then is silica II. The main chemical reactions have been given by formula 2 and 3.

Calcination stage:

$Na_2CO_3 \rightarrow Na_2O+ CO_2$

$Na_2O+4SiO_2 \rightarrow Na_2Si(Si_3O_9)$ (Formula 2)

$Na_2O+Al_2O_3 \rightarrow 2NaAlO_2$

$3Na_2O+4SiO_2+3Al_2O_3 \cdot 2SiO_2 \rightarrow 3Na_2O \cdot Al_2O_3 \cdot 2SiO_2$

Acid leaching stage:

$NaAlSiO_4+4HCl \rightarrow NaCl+AlCl_3+H_2SiO_3+H_2O$

$CaMgSi_2O_6+4HCl \rightarrow 2H_2SiO_3+CaCl_2+MgCl_2$

$CaFeSi_2O_6+4HCl \rightarrow 2H_2SiO_3+CaCl_2+FeCl_2$

(Formula 3)

As can be seen in Fig. 9, after acid leaching and alkaline leaching, the mixture by fly ash and sodium carbonate mixing and calcining is layer (sheet)-like structure, because quartz, illite, sodalite and sodium in slag react with carbonate at high temperature, and form nepheline and pyroxene which are layer (sheet)-like structure.

(5) Silica II

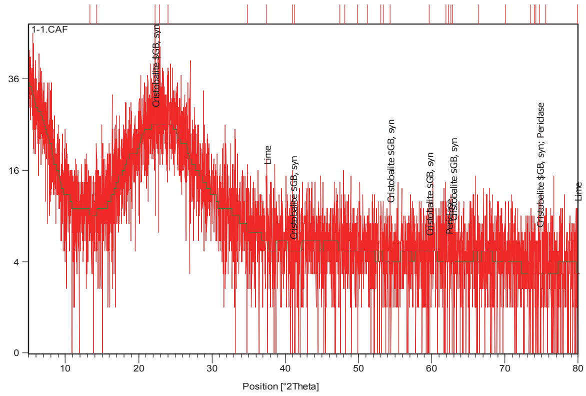

Fig. 10. X-diffraction patterns of silica II

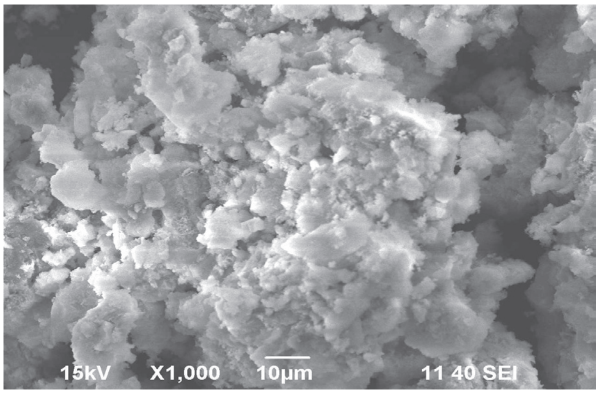

Fig. 11. SEM chart of silica II

Fig. 10 shows the X-diffraction pattern of silica II, and also the last remnants of this program. As can be seen from the figure, silica II makes a steamed bun peak between 2θ10～30, which shows its composition is mainly amorphous SiO_2, while there are still a small amount of crystallize minerals phase, such as quartz, periclase, but because of less quality, their impact would be smaller for the quality of silica II.

It can be seen by scanning electron micrographs of silica II: the product is disordered amorphous structure, and is similar with X-diffraction analysis. The size and shape of particle are different, two kinds of spherical and flaky, and there exists villous materials, which are similar to the reported in the literature [6].

4 CONCLUSIONS

(1) Determine the improvement programs through tests: acid leaching alkali leaching adding sodium carbonate and roasting second acid leaching, after improvement the maximum utilization of silicon, aluminum and iron are as follows: silicon 97.07 %, aluminum 86.67%, iron 96.54%.

(2) On the basis of experiments, designing the program about overall utilization of fly ash, which makes that a comprehensive utilization of fly ash is up to 100% (well-utilization is nearly 90%, the other 10% is used as building material additives). Chemical raw materials recycling saves the cost and obtain the response of energy efficiency and emission reduction.

(3) After first acid leaching, physical phase of quartz, glass state of alumina and magnetite do not change, while hematite is partial dissolved and changed into magnetite phase, while anhydrous gypsum, transparent feldspar, silica and spinel is also partial dissolved and changed into blue stone. Some active substance of amorphous mineral phase has been dissolved, besides, acid leaching destroyes the surface structure of fly ash particles, and increases the specific surface area, which is conducive to the follow-up reaction.

(4) After alkali leaching, amorphous SiO_2 is almost completely dissolved, blue square stone, glass state of alumina and magnetite change into illite and sodalite, which structure is relatively regular mineral phase(similar size, shape and smooth surface, spherical particles bond with each other), while quartz has not changed.

(5) Adding sodium carbonate and calcining, the others are changed into layer (sheet)-like structure of aragonite and a small amount of pyroxene, except less amount of quartz crystal.

(6) After second acid leaching, residues are mainly constituted by amorphous SiO_2, and mixed with a small amount of quartz, periclase impurities, this is one of the products about the program - silica II.

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