A further objective of the invention is to provide a method and plant for extracting one or more metals from fly ash utilising the method according to the invention for forming a suspension of partly dissolved fly ash in a mineral acid.

Summary

In one aspect, the present disclosure provides a method for forming a suspension of partly dissolved fly ash in an aqueous mineral acid solution, wherein the method comprises the following process steps:

1) supplying a mass, L, of an aqueous mineral acid solution to a dissolution reactor and then measuring and registering the initial temperature, T_0, and initial, pH_0, of the aqueous mineral acid solution,

2) set n = 1, where n is an integer, and select a target pH, pH_{targ}, to be reached in the suspension,

3) for n ≤ N, where N is an integer from 3 or higher, execute steps i), ii) and iii) in successive order:

i) adding and mixing an amount S_n of solid fly ash into the aqueous mineral acid solution,

ii) when the amount S_n is dissolved, measuring and registering the temperature and pH of the aqueous mineral acid solution at this n'th step as T_n and pH_n, respectively, and determining and registering an accumulated amount of fly ash, $S_{n,\,acc}$, being added to the aqueous mineral acid solution at this n'th step, and

iii) set n = n+1 and go to step i),

4) apply the registered temperatures T_0 to T_n and the registered pH-values pH_0 to pH_n, and the registered amounts of added fly ash, $S_{n,\,acc}$, and equations:

$$\Gamma_n^2 = \beta_1 - \beta_2 \Delta T_n \quad \text{and} \quad \Delta T_n = \gamma_1 \left(\frac{S_{n,acc}}{L}\right) - \gamma_2 \left(\frac{S_{n,acc}}{L}\right)^2,$$

where $\Gamma_n = 10^{-pH_n}$, $\Delta T_n = T_n - T_0$, and β_1, β_2, γ_1, and γ_2 are parameters, to determine the parameters β_1, β_2, γ_1, and γ_2 by regression analysis,

5) determining a total amount, S_{tot}, of solid fly ash to be added to the aqueous mineral acid solution from the relation:

$$S_{tot} = \frac{L}{2\gamma_2}\left[\gamma_1 + \sqrt{{\gamma_1}^2 + 4\gamma_2\left(\frac{\beta_1 - (10^{-pH_{targ}})^2}{\beta_2}\right)}\right],$$

and

6) if $S_{n,\,acc} < S_{tot}$, execute steps j) and jjj):

j) adding and mixing an amount S_n into the aqueous mineral acid solution,

jjj) if $S_{n,\,acc} < S_{tot}$, set n = n+1 and go to step j),

or else:

jjjj) stop feeding and mixing solid fly ash into the aqueous mineral acid solution.

In another aspect, the present disclosure provides a method for extracting one or more metals from solid fly ash, wherein the method comprises:

selecting a target pH, pH_{targ}, providing an optimized dissolution rate of those salts in the fly ash containing the one or more metals to be extracted and form a suspension according to the present disclosure,

passing the formed suspension to a separator separating the suspension into a solid fraction of undissolved fly ash and a first liquid fraction containing dissolved fly ash,

disposing the solid fraction of undissolved fly ash,

adding a base to the first liquid fraction to increase the pH to a level where one or more solved metals in the first liquid fraction precipitates as metal hydroxides,

passing the first liquid fraction with precipitated metal hydroxides to a separator separating the first liquid fraction with precipitated metal hydroxides into a solid fraction of precipitated metal hydroxides, and a second liquid fraction, and

collecting, and optionally passing the solid fraction of precipitated metal hydroxides to further processing.

In another aspect, the present disclosure provides a dissolution reactor for forming a suspension of partly dissolved fly ash in an aqueous mineral acid solution, comprising:

a reactor space adapted to receive and contain a mass, L, of the aqueous mineral acid solution at initial concentration, C_0, and initial pH_0,

a pH-sensor adapted to measure and register the pH in the aqueous mineral acid solution,

a temperature sensor adapted to measure and register the temperature of the aqueous mineral acid solution,

a supply of solid fly ash adapted to feed subsequent amounts ,S_n, of solid fly ash into the aqueous mineral acid solution in the reactor apace and to register the accumulated mass, $S_{n,\,acc}$, of solid fly ash being added,

a supply of aqueous mineral acid solution adapted to feed the amount L of aqueous mineral acid solution to the reactor space, and

a control unit, which is:

adapted to receive the registered the pH-values from the pH-sensor, the registered temperatures from the temperature sensor, and the registered accumulated mass, $S_{n, acc}$, of solid fly ash being added to the aqueous mineral acid solution, and which:

comprises a computer hardware with computer software containing instructions which when executed, utilise the registered pH from the pH sensor, the temperatures from the temperature sensor, and the registered accumulated mass, $S_{n, acc}$, of solid fly ash being added to determine the total amount of solid fly ash to be added to the aqueous mineral acid solution according to the method of the present disclosure, and which regulates the supply of solid fly ash to the aqueous mineral acid solution accordingly.

In another aspect, the present disclosure provides a plant for extracting metals from fly ash, comprising a dissolution reactor according to the present disclosure, further comprising:

a first separator adapted to separate the suspension formed in the dissolution reactor into a solid fraction of undissolved fly ash and a first liquid fraction containing dissolved fly ash,

a precipitation reactor adapted to receive the first liquid fraction,

a supply of a base adapted to add base to the first liquid fraction contained in the precipitation reactor,

a second separator adapted to receive the liquid fraction containing precipitated metal hydroxides and to separate it into a solid fraction of precipitated metal hydroxides and a second liquid fraction.

Description of the invention

The invention may be considered as a method for automatic regulation of the addition of solid fly ash to a mineral acid to achieve an optimized dissolution degree of the fly ash, and a reactor for executing the automatic regulation and obtain a slurry with an optimized content of dissolved metals to be extracted in downstream processing.

Thus, in a first aspect, the invention relates to a method for forming a suspension of partly dissolved fly ash in an aqueous mineral acid solution, wherein the method comprises the following process steps:

1) supplying a mass, L, of an aqueous mineral acid solution to a dissolution reactor and then measuring and registering the initial temperature, T_0, and initial, pH_0, of the aqueous mineral acid solution,

2) set n = 1, where n is an integer, and select a target pH, pH_{targ}, to be reached in the suspension,

3) for n ≤ N, where N is an integer from 3 or higher, execute steps i), ii) and iii) in successive order:

i) adding and mixing an amount S_n of solid fly ash into the aqueous mineral acid solution,

ii) when the amount S_n is dissolved, measuring and registering the temperature and pH of the aqueous mineral acid solution at this n'th step as T_n and pH_n, respectively, and determining and registering an accumulated amount of fly ash, $S_{n,\,acc}$, being added to the aqueous mineral acid solution at this n'th step, and

iii) set n = n+1 and go to step i),

4) apply the registered temperatures T_0 to T_n and the registered pH-values pH_0 to pH_n, and the registered amounts of added fly ash, $S_{n,\,acc}$, and equations:

$$\Gamma_n^2 = \beta_1 - \beta_2 \Delta T_n \qquad \text{and} \qquad \Delta T_n = \gamma_1 \left(\frac{S_{n,acc}}{L}\right) - \gamma_2 \left(\frac{S_{n,acc}}{L}\right)^2,$$

where $\Gamma_n = 10^{-pH_n}$, $\Delta T_n = T_n - T_0$, and β_1, β_2, γ_1, and γ_2 are parameters, to determine the parameters β_1, β_2, γ_1, and γ_2 by regression analysis,

5) determining a total amount, S_{tot}, of solid fly ash to be added to the aqueous mineral acid solution from the relation:

CLAIMS

1. A method for forming a suspension of partly dissolved fly ash in an aqueous mineral acid solution, wherein the method comprises the following process steps:

1) supplying a mass, L, of an aqueous mineral acid solution to a dissolution reactor and then measuring and registering the initial temperature, T_0, and initial, pH_0, of the aqueous mineral acid solution,

2) set n = 1, where n is an integer, and select a target pH, pH_{targ}, to be reached in the suspension,

3) for n ≤ N, where N is an integer from 3 or higher, execute steps i), ii) and iii) in successive order:

i) adding and mixing an amount S_n of solid fly ash into the aqueous mineral acid solution,

ii) when the amount S_n is dissolved, measuring and registering the temperature and pH of the aqueous mineral acid solution at this n'th step as T_n and pH_n, respectively, and determining and registering an accumulated amount of fly ash, $S_{n,\,acc}$, being added to the aqueous mineral acid solution at this n'th step, and

iii) set n = n+1 and go to step i),

4) apply the registered temperatures T_0 to T_n and the registered pH-values pH_0 to pH_n, and the registered amounts of added fly ash, $S_{n,\,acc}$, and equations:

$$\Gamma_n^2 = \beta_1 - \beta_2 \Delta T_n \qquad \text{and} \qquad \Delta T_n = \gamma_1 \left(\frac{S_{n,acc}}{L}\right) - \gamma_2 \left(\frac{S_{n,acc}}{L}\right)^2,$$

where $\Gamma_n = 10^{-pH_n}$, $\Delta T_n = T_n - T_0$, and β_1, β_2, γ_1, and γ_2 are parameters, to determine the parameters β_1, β_2, γ_1, and γ_2 by regression analysis,

5) determining a total amount, S_{tot}, of solid fly ash to be added to the aqueous mineral acid solution from the relation:

$$S_{tot} = \frac{L}{2\gamma_2}\left[\gamma_1 + \sqrt{{\gamma_1}^2 + 4\gamma_2\left(\frac{\beta_1 - (10^{-pH_{targ}})^2}{\beta_2}\right)}\,\right],$$

and

6) if $S_{n,\,acc} < S_{tot}$, execute steps j) and jjj):

j) adding and mixing an amount S_n into the aqueous mineral acid solution,

jjj) if $S_{n,\,acc} < S_{tot}$, set n = n+1 and go to step j),

or else:

jjjj) stop feeding and mixing solid fly ash into the aqueous mineral acid solution.

2. A method cording to claim 1, wherein step 6) further comprises step jj) to be executed after step j) and before step jjj):

jj) when the added amount S_n is dissolved, measuring and registering the temperature and pH of the aqueous mineral acid solution at this n'th step as T_n and pH_n, respectively, and determining and registering an accumulated amount of fly ash, $S_{n,\,acc}$, being added to the aqueous mineral at this n'th step, and then repeat steps 4) and 5) to provide a refined determination of S_{tot}.

3. A method according to claim 1 or 2, wherein the method further comprises stirring the aqueous mineral acid solution during the formation of the suspension of partly dissolved fly ash by use of an impeller or by gas stirring.

4. A method according to any preceding claim, wherein the amount S_n is determined by the relation:

$$S_n = \frac{S_{est}}{k}$$

where S_{est} is an estimate of the total amount of fly ash to be added, and k is an integer selected to be from (and including) 5 to (and including) 100, preferably from 7 to 75, more preferably from 10 to 50, and most preferably from 20 to 30.

5. A method according to claim 4, wherein when $n \geq \lfloor 0.75k \rfloor$, the amount S_n is determined by the relation:

$$S_n = \frac{S_{est}}{ak}$$

where a is an integer selected to be any integer from 2 to 10, preferably from 3 to 10, and more preferably from 5 to 10.

6. A method according to any preceding claim, wherein the estimate of total amount to be added, S_{est}, is determined by applying the acid balance:

$$S_{est} = \frac{L}{C_B}[C_0 - 10^{-pH_{targ}}],$$

where C_B is the concentration of dissolvable base in the solid fly ash.

7. A method according to of claims 4 to 6, wherein N is chosen to be an integer being equal to k/2.

8. A method according to any of claims 1 to 6, wherein the number N is any integer from (and including) 3 to (and including) 10, preferably from 4 to 8, more preferably from 5 to 7.

9. A method according to any preceding claim, wherein the aqueous mineral acid solution is hydrochloric acid or nitric acid, or a mixture thereof, having an initial pH ≤ 2, preferably ≤ 1.5, most preferably ≤1.0.

10. A method according to any preceding claim, wherein one or more oxidizing agents are added to the aqueous mineral acid solution, preferably O_3 and/or H_2O_2, the addition of one or more oxidizing agents is preferably made in step 1).

11. A method for extracting one or more metals from solid fly ash, wherein the method comprises:

selecting a target pH, pH_{targ}, providing an optimized dissolution rate of those salts in the fly ash containing the one or more metals to be extracted and form a suspension according to any of claims 1 to 10,

passing the formed suspension to a separator separating the suspension into a solid fraction of undissolved fly ash and a first liquid fraction containing dissolved fly ash,

disposing the solid fraction of undissolved fly ash,

adding a base to the first liquid fraction to increase the pH to a level where one or more solved metals in the first liquid fraction precipitates as metal hydroxides,

passing the first liquid fraction with precipitated metal hydroxides to a separator separating the first liquid fraction with precipitated metal hydroxides into a solid fraction of precipitated metal hydroxides, and a second liquid fraction, and

collecting, and optionally passing the solid fraction of precipitated metal hydroxides to further processing.

12. A method according to claim 11, wherein the base is chosen from one of; NaOH, KOH, $Ca(OH)_2$, CaO, or $Mg(OH)_2$, or a mixture of two or more thereof.

13. A method according to claim 11 or 12, wherein
the method further comprising:

mixing the second liquid fraction with solid magnetic particles having one or more adsorbents on their surface which selectively adsorbs the metal ions to be extracted,

feeding the mixture of magnetic particles and the second liquid residue to a magnetic separator separating the mixture into a fraction of magnetic particles and a third liquid fraction,

desorbing the adsorbed metal ions from the adsorbents on the magnetic particles and collect the desorbed metal ions as a product fraction,

disposing the third liquid fraction,

and optionally,

regenerating the one or more adsorbents on the desorbed magnetic particles.

14. A dissolution reactor for forming a suspension of partly dissolved fly ash in an aqueous mineral acid solution, comprising:

a reactor space ~~(1)~~ adapted to receive and contain a mass, L, of the aqueous mineral acid solution at initial concentration, C_0, and initial pH_0,

a pH-sensor ~~(2)~~ adapted to measure and register the pH in the aqueous mineral acid solution,

a temperature sensor ~~(3)~~ adapted to measure and register the temperature of the aqueous mineral acid solution,

a supply of solid fly ash ~~(4)~~ adapted to feed subsequent amounts ,S_n, of solid fly ash into the aqueous mineral acid solution in the reactor apace ~~(1)~~ and to register the accumulated mass, $S_{n,\,acc}$, of solid fly ash being added,

a supply of aqueous mineral acid solution ~~(5)~~ adapted to feed the amount L of aqueous mineral acid solution to the reactor space ~~(1)~~, and

a control unit ~~(6)~~, which is:

adapted to receive the registered the pH-values from the pH-sensor ~~(2)~~, the registered temperatures from the temperature sensor ~~(3)~~, and the registered accumulated mass, $S_{n,\,acc}$, of solid fly ash being added to the aqueous mineral acid solution, and which:

comprises a computer hardware with computer software containing instructions which when executed, utilise the registered pH from the pH sensor ~~(2)~~, the temperatures from the temperature sensor ~~(3)~~, and the registered accumulated mass, $S_{n,\,acc}$, of solid fly ash being added to determine the total amount of solid fly ash to be added to the aqueous mineral acid solution according to the method of any of claims 1 – 10, and which regulates the supply of solid fly ash ~~(4)~~ to the aqueous mineral acid solution ~~(5)~~ accordingly.

15. A dissolution reactor according to claim 14, further comprising an impeller ~~(7)~~ located in the aqueous mineral acid solution.

16. A plant for extracting metals from fly ash, comprising a dissolution reactor according to claim 14 or 15, further comprising:

a first separator ~~(8)~~ adapted to separate the suspension ~~(9)~~ formed in the dissolution reactor ~~(1)~~ into a solid fraction ~~(10)~~ of undissolved fly ash and a first liquid fraction ~~(11)~~ containing dissolved fly ash,

a precipitation reactor ~~(12)~~ adapted to receive the first liquid fraction ~~(11)~~,

a supply of a base ~~(13)~~ adapted to add base to the first liquid fraction ~~(11)~~ contained in the precipitation reactor ~~(12)~~,

a second separator ~~(14)~~ adapted to receive the liquid fraction containing precipitated metal hydroxides ~~(15)~~ and to separate it into a solid fraction ~~(16)~~ of precipitated metal hydroxides and a second liquid fraction ~~(17)~~.

17. A plant according to claim 16, further comprising:

a supply of magnetic particles ~~(19)~~ having one or more metal ion adsorbing adsorbents on their surface,

a mixing tank ~~(18)~~ adapted to receive the second fluid fraction ~~(17)~~ and magnetic particles from supply of magnetic particles ~~(19)~~ and to mix the liquid and particles,

a magnetic separator ~~(22)~~ adapted to receive the mixture ~~(21)~~ of the second liquid fraction and magnetic particles, and to separate the mixture ~~(21)~~ into a solid fraction ~~(25)~~ of magnetic particles and a third liquid fraction ~~(24)~~, and optionally,

an impeller ~~(20)~~ located in the mixing tank ~~(18)~~.

18. A plant according to claim 16 or 17, wherein the magnetic particles:

have a mean particle size, d_{50}, in the range of from 10 nm to 10 µm, preferably from 50 nm to 5 µm, and most preferably from 100 nm to 1 µm, and

are either ferromagnetic, ferrimagnetic, superparamagnetic, or combinations of these properties.