Projektowanie przemysłowych instalacji do krystalizacji z roztworu na przykładzie technologii siarczanu amonu

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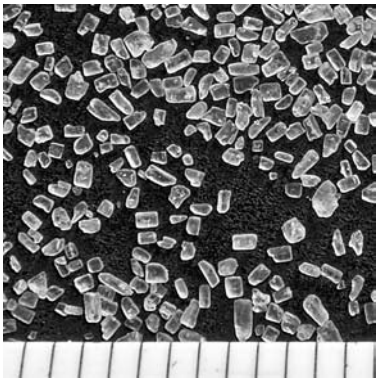
Streszczenie

W artykule omówiono ilościowe i jakościowe rozpoznanie najistotniejszych zagadnień, niezbędnych przy projektowaniu nowych instalacji przemysłowych, w przypadku, kiedy nie dysponujemy danymi ruchowymi z innych podobnych technologicznie układów. Jako przykład wykorzystano instalację do produkcji krystalicznego siarczanu amonu przeznaczonego dla rolnictwa. Surowcem do produkcji był roztwór (zawiesina) siarczanu amonu powstała w procesie odsiarczania spalin metodą amoniakalną. Wdrożona technologia umożliwia produkcję 60 tys. t/r nawozowego siarczanu amonu spełniającego Dyrektywę Unijną nr 1107/2008, z dnia 07.11.2008

Słowa kluczowe: krystalizacja przemysłowa, siarczan amonu, FGD, CFD



Krystalizacja przemysłowa

Designing of industrial crystallization plants in the light of ammonium sulphate technology

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Introduction

The paper describes an industrial application of spent liquid utilization from ammonia water after flue gas desulphurization (FGD) by crystallization from solution [1]. The discussed method concerns ammonium sulphate (AS) production. Basing on the technology described in this paper the ammonium sulphate fertilizer of the average size of 0.6 mm can be manufactured in an economical way. The product meets qualitative requirements of the European Union Directive No. 1107/2008, dated 07.11.2008.

In the paper several aspects are discussed: (i) the results of laboratory preliminary experiments, (ii) CFD (Computational Fluid Dynamic) calculations of a proposed technology, (iii) process solution for final product yield *i.e.* 60 000 ton per year of AS fertilizer and characteristics of AS crystals, respectively.

The proposed method does not generate any wastes and gives another advantages like: (i) the possibility of change of the very expensive low sulphur fuels to cheaper high sulphur fuels in existing boilers, (ii) the higher the SO_2 content in the fuel gas the higher output of the fertilizer and revenue stream is generated. The revenue from the sale of ammonium sulphate very quickly compensates the investments costs.

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Technological background

The process of AS crystallization from solution as a result of the absorption of the exhaust gases in ammonia water differs from the popular crystallization of AS from solution like after the caprolactam ($C_6H_{11}ON$) production [2, 3].

The complexity of this process is caused by the dissimilarities in the crucial factors. The main significant differences are as follows:

- raw material consists of: 40% w/w of the AS suspension with ash addition of up to 0.3% w/w
- multi-component solution, depending on the combustion grade of coal, contains up to the 43% w/w of AS, up to the 3% w/w of ammonium chloride, up to the 2.5% w/w of ammonium nitrate and up to 0.9% w/w of ammonium fluoride
- very changeable scale of the fertilizer production during the year, which depends on seasonal thermal energy efficiency of power station and is in the range of
- 40–125 per cent with respect to the nominal load
- chemical composition of the feed provided to the crystallization unit changes with time because of instability of the absorption unit. The absorption parameters changes as well as properties of components, in particular because of ammonium fluoride decomposition at higher temperature. To avoid uncontrolled ammonia emission and to limit corrosion the pre-treatment of feed solution with calcium soluble species solution is required

- Ammonium chloride and ammonium fluoride present in a feed strongly affect the corrosion rate
- Presence of ash particles in a feed solution forced an additional filtration step in order to protect pumps against sealing damage.

The above mentioned reasons and their negative effect on a process force to treat this issue in a special manner.

Small scale investigation

The laboratory scale investigations in a typical 2 litres of volume set-up were carried out. The tests were mainly focused on basic kinetics constants determination as well as on description of the relation between residence time, unit power input and particle size distribution (PCD).

The values of investigated constants like: G_{ef} and B_o are equal to (1.47–0.667)10^{-7} m/s and (637–0.046)10^{10} 1/(m^{3}s), respectively. Ammonium sulphate crystals reach satisfactorily large value of the G_{ef} and comparatively low value of the B_o. It proves that crystallization process goes easily and one may get the product close to 0.7 mm of mean size in a relatively short period of time. For that reason we also suppose that, in an industrial scale, the SFL (**S**emi **F**luidised **C**rystallizer) crystallizer reaching lower *CV* value is also highly possible to apply. In the range of particles smaller than 200 microns the deviation from the linear population density distribution confirms that the crystals attrition occurs.

Interesting are results showing effect of the residence time on mean particle size and relation between unit power input and average size. Increase in residence time has a weak influence on an average particle size, $L_m \alpha \tau^{0.16}$. On the contrary, "more" effective was the influence of unit power input on a mean size, $L_m \alpha \tau^{-2.82}$.

Additionally, the relative large effect of unit power input on nucleation rate was found, $B_0 \alpha \tau^{8.01}$. It means that unit power input should be very precisely determine in order to control level of the nucleation rate in case when medium sized crystals are crystallized.

CFD simulations

For the given product requirements, product yield and having some crystallization kinetic data from the lab scale, the design of an industrial scale SFL crystallizer was commenced. In the range of this issue the fluid dynamic parameters as well as geometrical proportion of the crystallizer body by means of CFD procedure [4÷6] had to be determined.

The main task was the determination of the following data: (i) the axial fluid velocity distribution in the annular zone of apparatus, (ii) volumetric suspension distribution in the SFL crystallizer.

The CFD numerical calculation was based on finite volumes method.

An axial velocity distribution plays a dominant role in hydraulic classification of solids. At the top of the bed an axial velocity is "responsible" for the amount of small crystals washed out from the bed to the outer circulation loop. At the bottom of apparatus the axial velocity determines the product size, which is withdrawn to the centrifuge. Profile of axial velocity distribution clearly shows that suspension inside the apparatus is far from fluidized. Suspended particles behaviour is closer to fountain-like than to fluidized bed. So particles in this case are not well classified and thus it is almost impossible to obtain a narrow range sized product with out additional classification in a elutriation leg under the apparatus bottom.

The local volumetric concentration distribution of particles in suspension in the discussed type of apparatus is shown in Figure 1. The volumetric concentration distribution is not uniform. The lower concentration values are located on the central part of bed. In the area where a stream of circulated solution is coming from the central pipe the concentration of particles is very low so the risk of circulation blocking is very small. But in this case the product pipe connector should be located slightly higher than usually. Our industrial observations prove this statement. The density of the bed measured in industrial crystallizes by means of isotopic densimeter shown some changes in function of the bed height. The maximum value of a suspension density was found close to the wall dozens of centimetres above a tank bottom.

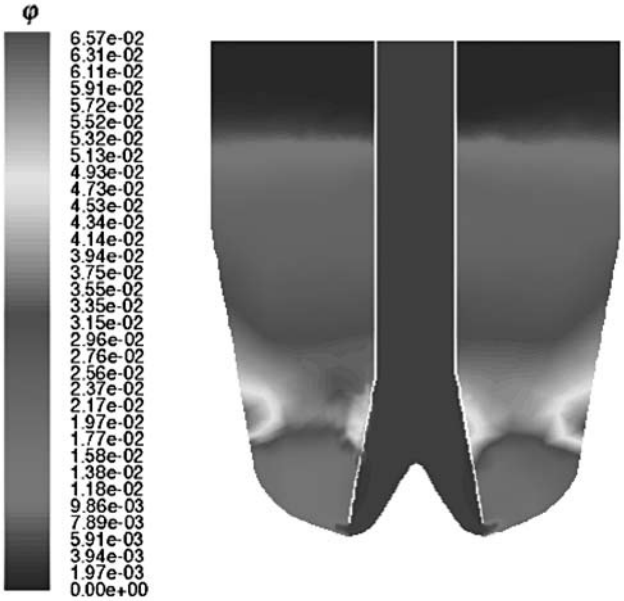

Fig. 1 Volumetric particles distribution φ, for particle mean size *L*=0.4 mm, apparatus diameter *D*=3m

Generally, the volumetric suspension distributions in the apparatus determined by means of the CFD simulation method were consistent with measured local suspension density in the industrial scale. The suspension density was determined using isotopic densimeters located in various places inside the industrial apparatus.

Industrial product analysis

The final product consists of two components [7] *i.e.* fine crystals from FGD ammonia process and mean sized from isothermal two-stages evaporative crystallization (Fig. 2.). In this case, the kinetics of those two components crystallization are based on completely different phenomenon. The first one comes from chemical reaction between ammonia water and flue gases, while the second source of product is a result of physical process with partial hydraulic classification of crystals. These kinetic differences and different principles of operation of the reactors have a strong influence on final product CSD. Generally AS particles generated in the FGD process do not achieve mean size of 0.3–0.4 mm . In order to get the final product in the range of 80% in 0.3–0.8 mm of size the two SFL crystallizers were designed to obtain product characteristic with average particle size around 0.7mm and 95% of the crystals population above 0.3 mm. The effective linear growth rate generated in the SFL crystallizer is in range of G_{ef} (8.0–7.5)·10^{-9} m/s while nucleation rate reaches value of B_0 (1.60–0.15)·10^8 1/(m^{3}s). The B_0 and G_{eff} data were determined for the some supersaturation of solution as in the laboratory conditions. The G_{ef} value in industrial scale is more or less three times lower than in laboratory scale but nucleation rate is still on the same level. The industrial crystallizer operated at the same level of solution supersaturation and unit power input as generated in the laboratory conditions. The feed in the laboratory solution was prepared from main components *i.e.* ammonium sulphate, ammonium nitrate, ammonium chloride and ammonium fluoride, where in the final scale we were working with a real solution from absorption unit. In our opinion, this difference of the feed composition mainly affects lengthening of growth rate value.

The attrition takes place also in industrial scale. This phenomenon was observed in the range of small crystals (less than 200 microns).

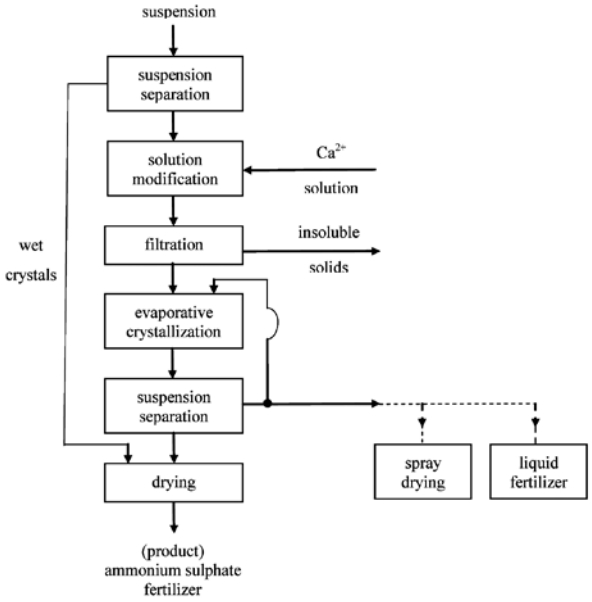

Fig. 2. Block diagram of ammonia sulphate production

The sample of AS particles, taken from industrial SFL apparatus, is shown in Photo 1.

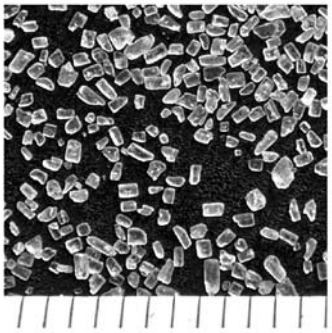

Photo 1. Ammonium sulphate crystals from the industrial SFL crystallizer (1 mm scale)

In Table 1 some data, describing characteristic of the obtained product are collected

Table 1

Product characteristic

Parameter	Product from SFL crystallizer	Final product characteristic
mean particle size , mm	0.69	0.40
particle range, mm	3.9% < 0.3 60% (0.3-0.8) 36.1% > 0.8	28.5% < 0.3 69% (0.3-0.8) 2.5% > 0.8
variation coefficient *CV* , %	46	71
concentration of ammonium nitrogen in the fertilizer, %w/w		> 20

Conclusions

During our tests in the lab as well as in industrial scale, it was confirmed that the determination of growth rate strongly depends not only on the main components concentration in solution, solution supersaturation, power input and kind of apparatus but also on the contaminations in feed solution in the real process and chemically not stable enough feed. The growth rate in the laboratory experiments for the same power input, supersaturation of solution and main composition of solution was almost three times bigger than reached in industrial application. So the design based only on laboratory data may be very crucial especially when the spend liquids are utilised.

The CFD computation method supports the designing procedure very well. Results of simulations for industrial scale are consistent with observation of the fluidized-bed behaviour in the real SFL crystallizer. Calculated solid concentration distribution was proved by means of *in-situ* local density measuring. The numerically determined zones of high concentration of suspension in reality were also found.

The described industrial process enables the production of the AS fertilizer of a guaranteed quality complying with the EU requirements No. 1107/2008.

Technology, in optional large scale, economically manufactures the crystalline product of the average size of $L_m \leq 0.6$ mm and total ammonium nitrogen concentration above 20 per cent.

The method is a competitive alternative to the traditional FGD solution based on lime stone, as after the process one gets the top commercial fertilizer grade by-product.

It is worth mentioning, that the developed technology is being successfully implemented on full scale in one of the Polish chemical factories. The design capacity of the plant is 60 000 tons of AS crystals per year.

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