Crystal Growth of Calcium Carbonate with Various Morphologies from Residual Calcium Chloride Solution

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It is known that chemical industry is not the principal pollution, but with all that its public image is still unfavorable. For changing the wrong image about chemical industry it is necessary to present the real possibilities of this domain in the problems of environment protection. To this purpose the present paper wants to serve, because it proposes the obtaining of calcium carbonate, which is used in different industries, on the base of inorganic industry of high tonnage (the industry of soda ash). In this case, the paper analyzes the influence of some parameters on the morphology and granulometric of calcium carbonate. The morphology of the calcium carbonate particles was characterized with scanning electronic microscopy (SEM). The size of particles was obtained by laser analyses. Results of research have shown that the production of ultrafine calcium carbonate based on residual solution from soda ash is possible. The shape of particles depends on the ratio of reactants, revolution influencing their dimension. The new products achieve the standards necessary for filler of rubber, paint and pigment industries. The additional advantage of the described methods is not only obtaining ultrafine calcium carbonate precipitation, but also reducing waste dangerous for the natural environment. Soda ash factories may also benefit from the introduction of the technology (sale of ultrafine calcium carbonate, release from environment pollution fees).

Keywords: waste, capitalization, calcium carbonate, morphology, particle size

One of the major problems of contemporary society is the environment pollution. Economical and demographical growth, the increasing consumption of goods and services has resulted to an explosion of wastes which are eliminated in the environment [1].

Maintaining a reasonable rhythm of socio-economical development is not possible without considering the environment an exhaustible source. The quality of environment for the next generations depends in a great measure of the way in which the specialists engaged in sphere of production, consuming, in this case the chemical engineers know how to respond to the imperatives of contemporary world [2].

In the process of conversion of raw material in finite product and subsequent, in the consuming and utilization phase, the assembly of materials are generated (inert, deleterious and even dangerous), usually named wastes, that can not be transformed in useful products, transferring to the nature the problem of their reprocessing. The environment, in which all the phases of complex process of transformation of raw material into waste, represents the source of all entrances and the deposit of all exits [3, 4]. The wastes can contain value components and by identification of socio-economical necessities which are pointed out on the market of end product in the marketing phase, it can realize incorporated processes for transforming the existing raw materials by supplying of some products asked by the market.

For example it was chosen to analyze the process of obtaining the soda ash. The ammonia Solvay process, conceived and realized in 1872s, when the restrictions were minimum, ensures the transformation, with a great wastage of raw materials, of sodium chloride and lime into soda ash. This classical process, well incorporated from the point of view of ammonia and power carriers, eliminates as residual solutions 25% from sodium, 100% from calcium and chloride introduced by raw materials. To this other pollution flux are added such as: alkaline slimes from purifying and regeneration (about. 200-450 kg /t soda), 80 m^3/t warm water soda, 800-1000m^3 N /t soda of burnt gases [5, 6]. As a consequence of these eliminated fluxes the classical process is much polluted and constitutes one of the principal responsible of undesired image of chemical industry in contemporary society.

The occurrence of request for ammonia chloride, that exists as dissolved form in the filters solution, at the begin of sixties it has resulted in the appearance of the new ammonia process, developed by the firm ASAHI GLASS, that allows the obtaining simultaneously the soda ash and ammonia chloride fertilizer. With the decreasing of request of ammonia chloride fertilizer this suddenly transformed from end product into by-product. The occurrence of this phenomenon on the market of end products has imposed the changing of DUAL technology, for processing the ammonia chloride, putting good use to ammonia.

The technological solution appeared as new process ASAHI GLASS, presented in figure 1, essentially consisted of transforming the ammonia chloride into calcium chloride, by its dissolution with lime.

The obtained ammonia is recycling in the ammonia phase and the solution of calcium chloride is processed by physical process being transformed into products required on the market.

The possibility of simultaneously production of more products required on the market made that in the conditions of observance of the ecological restrictions The NEW

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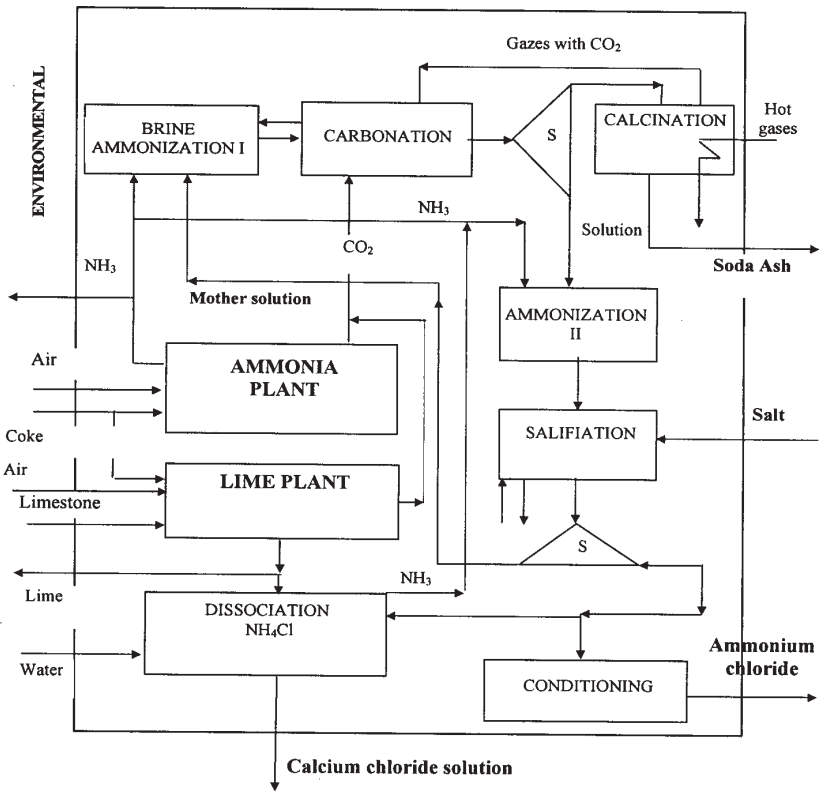


Fig 1 Block scheme of NEW PROCESS ASAHI GLASS

PROCESS ASAHI GLASS to be more flexible to requirements and so more viable than its predecessor.

The residual solution waste dangerous for the natural environment can be used to obtain precipitated calcium carbonate of a standard value [7].

The demand for precipitated calcium carbonate has been rapidly growing in recent years in various fields of industry (e.g., paper, rubber, plastics and paint industries as a coating pigment, filler or extender, food and horticulture) [8, 9]. Therefore, the precipitation of calcium carbonate has received much attention in the literature. Its application is determined by the great number of strictly defined parameters, such as average particle size, particle size distribution and morphology, specific surface area, brightness, oil adsorption, chemical purity, etc. Two of the most important has average particle size and morphology [10].

Synthesis of calcium carbonate precipitate (CCP) followed by two basic synthetic routes [11-14]: (1) the solution route, through a double decomposition reaction, wherein aqueous $CaCl_2$ and Na_2CO_3, or $CaCl_2$ and $(NH_4)_2CO_3$, or $Ca(NO_3)_2$ and Na_2CO_3 are combined in an equal molar ratio; and (2) the carbonation method, in which CO_2 gas is bubbled through an aqueous slurry of $Ca(OH)_2$. Many studies have shown that the properties of PCC, such as the particle size and shape, depend strongly on the preparation methods and conditions [15, 16].

Preparation of CCP in the presence of all kinds of organic substrate or other doubly charged ions using soluble carbonate and calcium salts as initial materials has been extensively reported [17-20]. Depending on the conditions of precipitation they may be either rosette (scalenohedral), blocky (rhombohedral), or various intermediate types. It is also possible to precipitate the aragonite crystalline form of calcium carbonate, and such particles tend to be needle-like (acicular).

Formation of a solid phase from a supersaturated solution is initiated through primary and secondary nucleation. When dealing with precipitation at higher supersaturation, it is often assumed that the effect of secondary nucleation is negligible.

As can be seen from the relationship derived from the classical nucleation theory, the nucleation rate depends on the interfacial energy, temperature and supersaturation. So four independent parameters on the average particle size of calcium carbonate precipitation taken into consideration are as follows [7, 21]:

- the concentration of reactives;
- mixing processes of solutions added to the reactor ;
- time of reactant settling in the reactor;
- temperature of the reaction process.

In this study, particles were synthesized by solution route, through aqueous $CaCl_2$ and Na_2CO_3. Without other doubly charged ions, we will primarily focus on studying the order to adding the reactives and the ration of this, in the initiating the nucleation of calcium carbonate precipitate (CCP) particles, as is expected role in calcium carbonate polymorph formation. This idea is potentially important for industrial process where nucleation control is a critical factor. The influence of ratio reactives is important for the regulation of growth of calcium carbonate and the resulting specificity of crystal morphology and particle aggregation.

Experimental part

For samples obtaining was used $CaCl_2$ solutions in concentration of 80, 165, 250 g/L and Na_2CO_3 solution in concentration of 90, 140, 190 g/L. Stirring time was 30 min at 500 rev/min and it was used an excess of 0.5% CO_3^{2-} comparing with stoichiometric Ca^{2+} quantity [8].

By experimental design the conditions of working presented in Table 1 were chosen.

During the precipitation and stirring processes, the reactive systems were kept at a certain temperature. At the end of each crystallization experiment, the precipitated solids were collected by filtering through G4 funnel (6 mm), and rinsed four times with doubly deionized water. Finally, the $CaCO_3$ precipitates were dried in desiccator cabinet at 100 ^{0}C for 2 h, and used for measurements.

Table 1
CONDITION FOR PCC OBTAINED

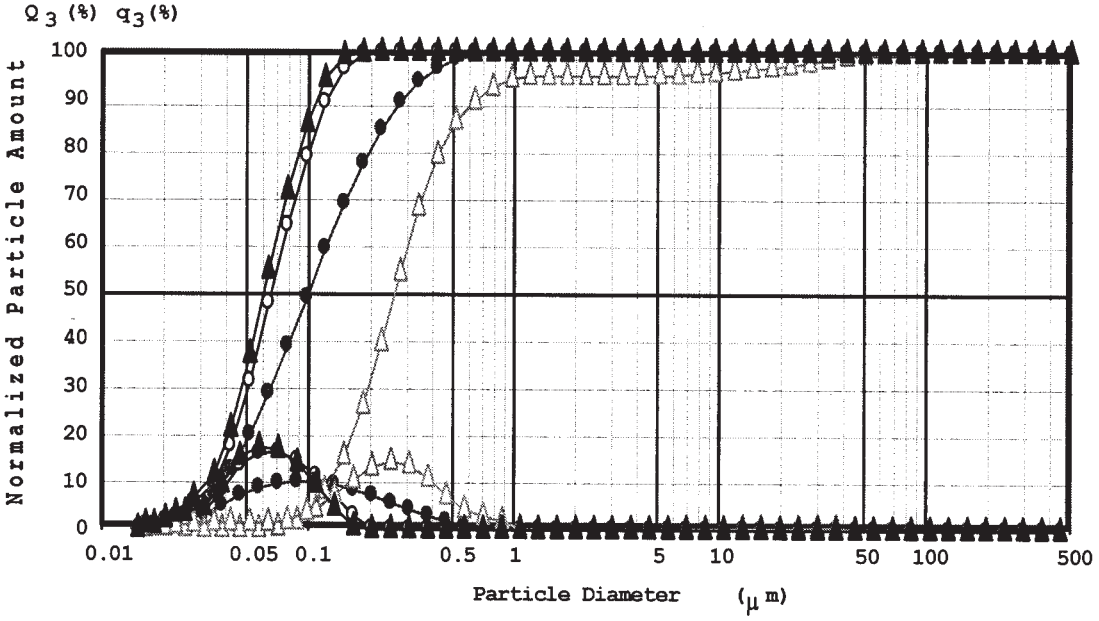
Sample	Parameters			Speed	Ration
	$c°_{CaCl2}$ g/L	$c°_{Na2CO3}$ g/L	T, C	rpm	
CCP1	80	90	30	500	0.88
CCP2	250	90	30	500	2.77
CCP3	80	190	30	500	0.42
CCP4	250	190	30	500	1.31
CCP5	80	90	80	500	0.88
CCP6	250	90	80	500	2.77
CCP7	80	190	80	500	0.42
CCP8	250	190	80	500	1.31
CCP9-12	165	140	55	100	1.17

The resulting $CaCO_3$ particles were characterized by scanning electron microscopy (SEM) (type Vega Tescan) with an accelerating voltage of 30 kV. SALD-7001 with laser was used to characterize calcium carbonate average particle size.

Results and discussion

The preliminary studies [10] have demonstrated that hydrodynamic influences the granulomeric distribution of particles. The increase of stirring speed determines the decrease of medium diameter of particles

In the paper the stirring speed were of 500 rot./min for synthesizing ultra fine calcium carbonate. The obtained experimental results are presented in figure 1.



	Median D	Modal D	Mean V	Std Dev	25.0%D	50.0%D	75.0%D
1	0.066	0.058	0.065	0.213	0.047	0.066	0.093
2	0.101	0.108	0.102	0.331	0.059	0.101	0.176
3	0.262	0.250	0.310	0.493	0.179	0.262	0.394
4	0.061	0.058	0.060	0.203	0.044	0.061	0.084
5							
6							
7							
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9							
10							
11							
12							

Fig. 2. Granulometric distribution

Data presented in figure 2 demonstrate that synthesized CCP has medium diameter of particles under 0.3 micrometers, so it can be successfully used as filling material.

Near the granulometric distribution a special importance has for users the shape of particles. Preliminary studies [8] have demonstrated that function of technological parameters it results the spherical particles, rhombic particles and spherical and rhombic particles mix. For that, in the conditions of maintaining the constant stirring speed the studies were extended for establishing the influence of parameters for synthesis of CCP of imposed morphology. The study of morphology was realized on the base of SEM analyze. For the beginning the influence of initial solutions was followed (fig. 3).

By analyzing SEM pictures presented in figure 3 it can observe that o relation between solutions concentrations and CCP morphology cannot be established. But, it is obviously that the morphology depends on the reactors ratio, more precisely of the ratio between the calcium ions concentration and carbonate ions concentration. The shape of CCP particles function the ratio $[Ca^{2+}]/[CO_3^{2-}]$ is presented in figure 4a-d.

The centralized data concerning the morphology function of the ratio of reactors are presented in table 2.

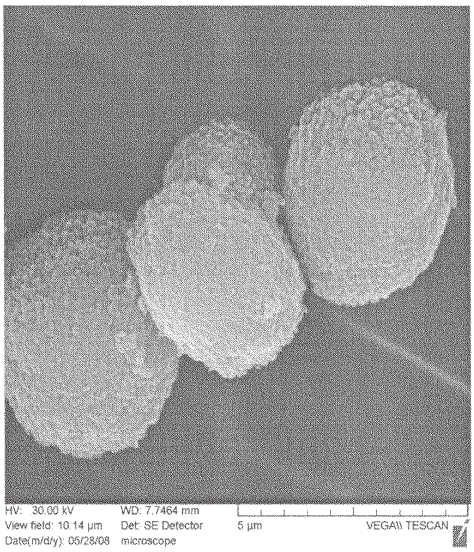
From SEM pictures given in figure 3.a-d and data given in table 2 it can observe the followings: the particles have rhomb shape (calcite) in the cases of ratios $[Ca^{2+}]/[CO_3^{2-}] < 0.5$ and $[Ca^{2+}]/[CO_3^{2-}] > 2$.

In the case of ratios with values around 1 (0.88-1.31) the particles of spherical shape result at temperatures of about 30^0C and particles of mix of shape for temperatures of 80^0C.

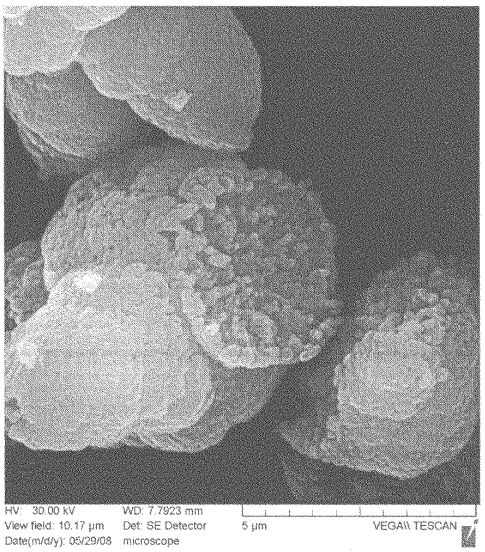
Also, it was observed that for the ratio 1.17 and 50^o C the particles of rhomb shape were obtained with nanoparticles of spherical shape. On the base of these observations it can be concluded that the temperature increase determines the transformation of vaterite form into calcite form.

The results obtained demonstrate that spherical particles are obtained by aggregation of nanoparticles of calcium carbonate (fig.5).

- **diluted solutions with calcium chloride**

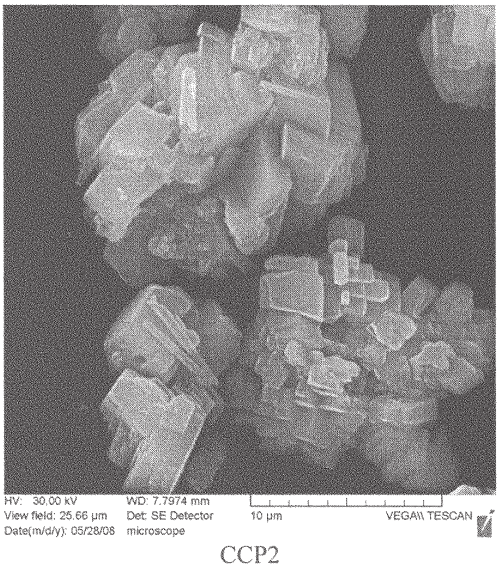


CCP1

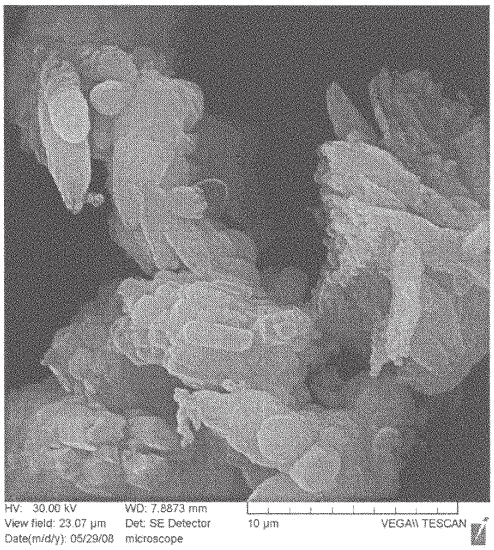


CCP5

- **concentrated solutions of calcium chloride**

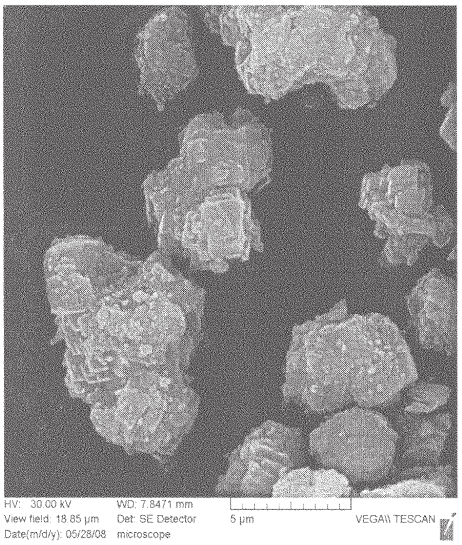


CCP2

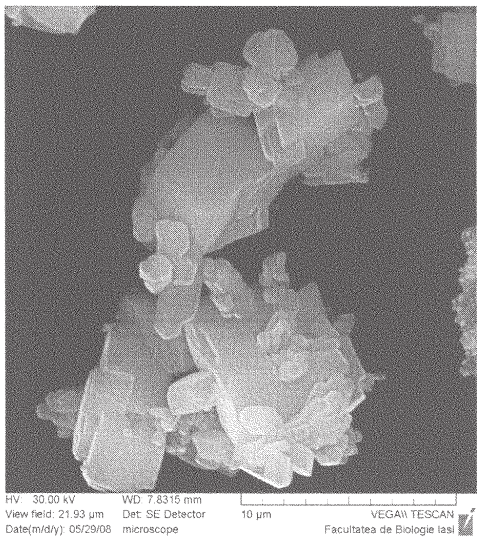


CCP6

- **diluted solutions of sodium carbonate**

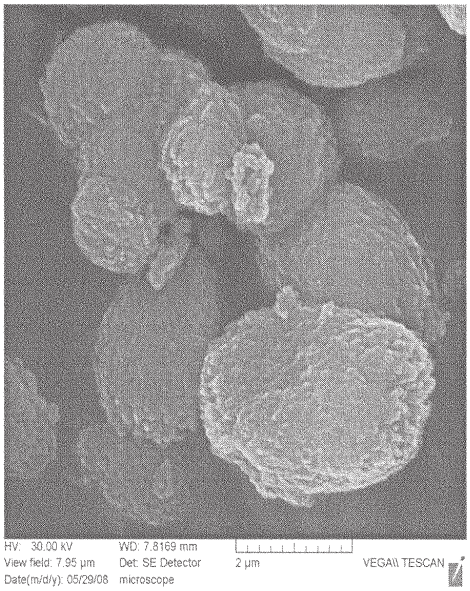


CCP3

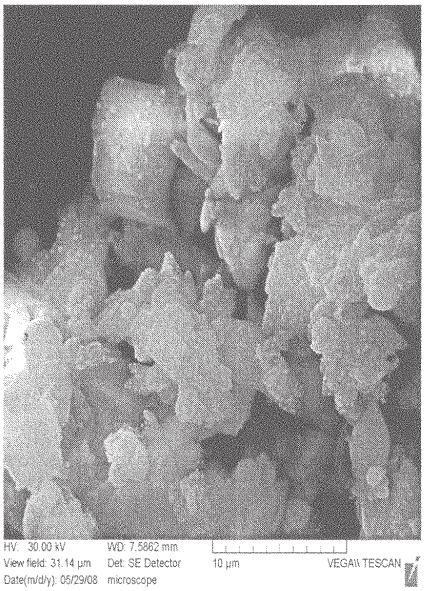


CCP7

- **concentrated solutions of sodium carbonate**

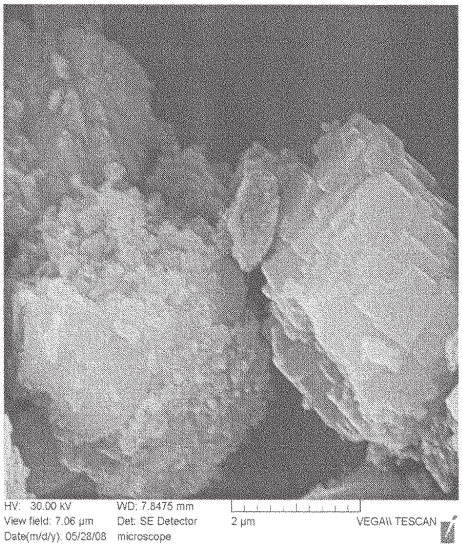


CCP4



CCP8

Fig. 3. Influence of solutions concentrations on CCP morphology



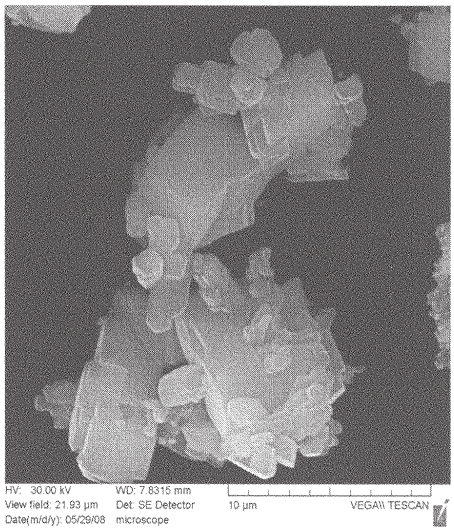


Fig . 4.a. SEM for 0.42 ratio

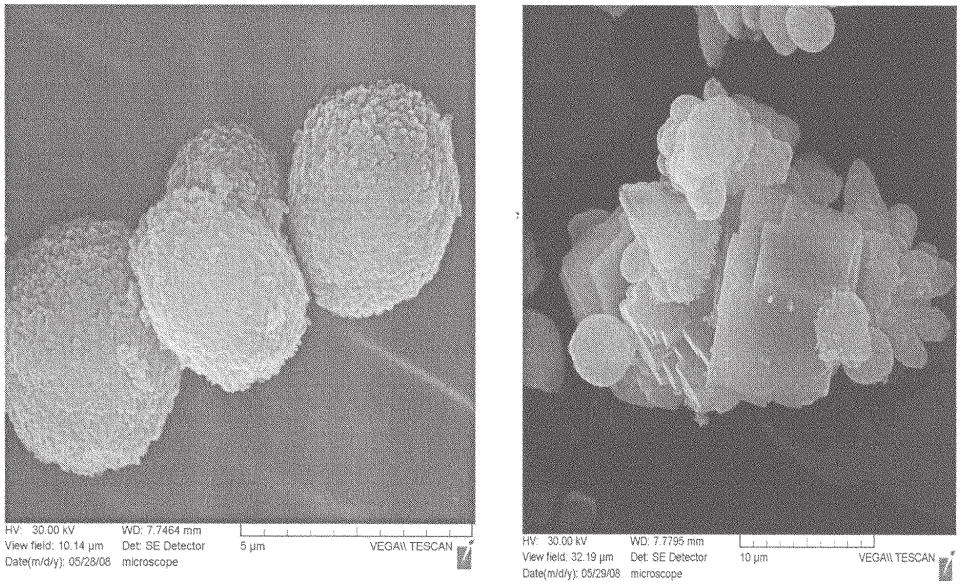


Fig . 4.b. SEM for 0.88 ratio

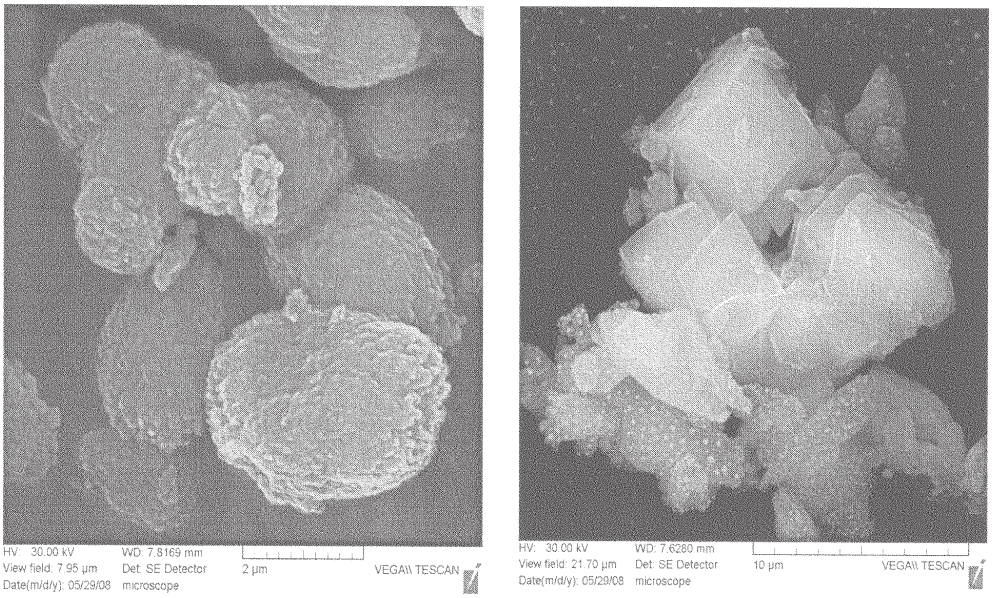


Fig. 4.c. SEM for 1.31 ratio

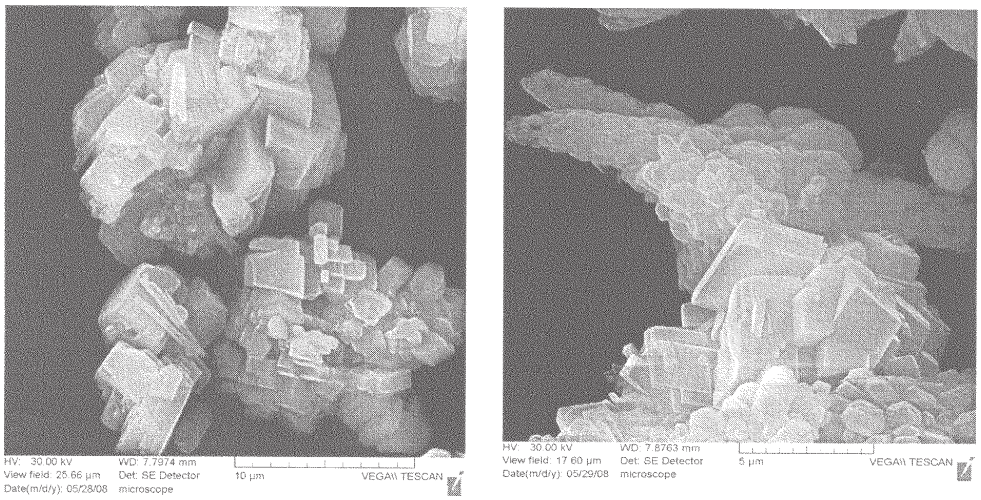


Fig. 4.d. SEM for 2.77 ratio

Ratio	T	Shape
0,42	30	Rhomb
	80	Rhomb
0,88	30	Spherical
	80	Mix
1,31	30	Spherical
	80	Mix
2,77	30	Rhomb
	80	Rhomb

.Table 2
INFLUENCE OF RATIO $[Ca^{2+}]/[CO_3^{2-}]$

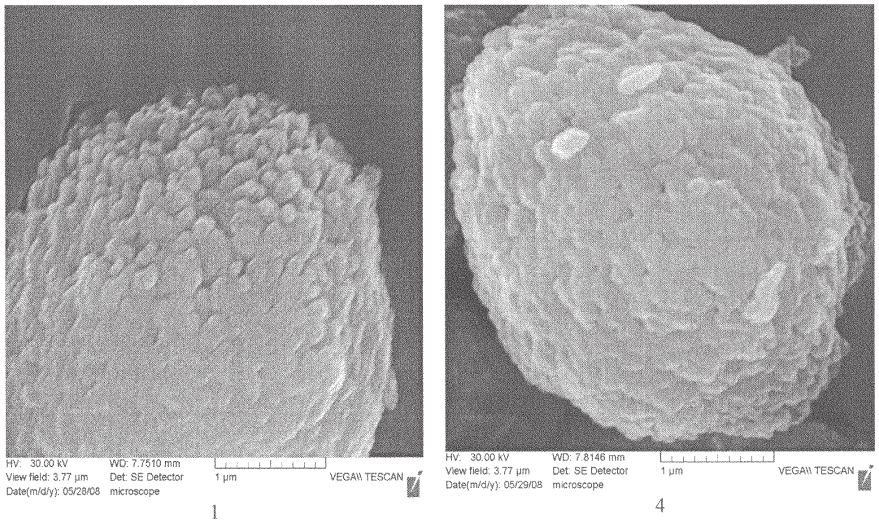


Fig. 5. Shape of spherical CCP particles

Conclusions

These research results demonstrate that the production of spherical ultrafine calcium carbonate precipitation can be undertaken to ''solve'' the waste utilization problems in the soda ash industry. It can reduce the negative influence of soda factories on the natural environment.

In the given experimental conditions the precipitated calcium carbonate results, having a medium diameter smaller than 0.5 micrometers, as it was observed in granulometric distributions.

Function of working conditions it results spherical particles, rhomb particles and a mix of spherical and rhomb particles.

The obtained results show that spherical particles are resulting by aggregation of nanoparticles of calcium carbonate.

The CCP morphology depends on the reactors ratio, more precisely on the ratio between the concentration of calcium ions and the concentration of carbonate ions

From SEM pictures it can observe that: the particles have rhomb shape in the case of ratios $[Ca^{2+}]/[CO_3^{2-}] < 0.5$ and $[Ca^{2+}]/[CO_3^{2-}] > 2$. In the case of ratios around the value 1 (0.88-1.31) the spherical particles result at a temperature of 30^{0}C and a mix of particle shape for temperature of about 80^{0}C.

Also, it was observed that for the ratio 1.17 and 50^{o}C the rhomb particles with nanoparticles of spherical shape resulted.

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Manuscript received: 15.06.2009