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Production and concentration of fine colloidal silica by electrodialysis

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ABSTRACT

The aim of our experiments was to verify the possibility of preparation and concentration of colloidal silica using an electrodialysis unit and membranes RALEX®. The experimental conditions for the preparation of initial solution suitable for electrodialysis by utilization of phosphoric(V) acid were optimized. A proper control during the following concentration steps was suggested and a fine high-purity colloidal solution of concentration up to 10 % w/w (SiO_2/water) was successfully prepared. Concentrated solution evinced good long-term stability. Phenomenon that provides stabilization during concentration step is described. We have observed that pH control during electrodialysis process is crucial to prevent membranes clogging and influences overall stability at laboratory condition. Size characterization of the colloidal system was carried by dynamic light scattering. Measured average particles size of colloidal solution was 9 nm.

Keywords: Colloidal silica; Electrodialysis; Stability; Concentration; Sodium silicate

1. Introduction

Colloids are defined by IUPAC [1] as particles (solid, liquid or gas) which colloidal sizes range from 1 to 1,000 nm and are dispersed in a continuous phase of a different composition (state). Colloidal silica is then here taken as highly polymerized particles of polysilicic acid larger than 5 nm stabilized in a liquid phase (water). The origin of colloidal silica comes down to the end of the 19th century, since when colloidal silica market started to continuously grow and the growing trend is expected to maintain far more in the future, especially thanks to new applications which are invented almost every day. Previous applications such as thin film coatings [2], binding [3] and polishing agents [4], catalyst material [5], etc., are still utilized, so there is worldwide need for silica supply. New advancement in technology requires highly concentrated colloidal silica with colloidal particles whose sizes do not exceed 12 nm. Such silica is then taken as a fine or high-quality silica.

Industrial production of sufficient amount and high quality of the colloidal silica is nowadays done with use of ion-exchange columns [6]. As the starting material, typically an alkali-silicate diluted solution is used and it has to be partially neutralized initially, leading to the formation of silica particles (or nuclei). The sodium residues are then removed by ion-exchange columns and diluted colloidal silica is then produced. Following final concentration step is carried by an evaporator. Regardless of the complexity of the production, the evaporation belongs to the most expensive step. The quality of the product decreases because of the continuous exhausting of the ion-exchanger. Also, regeneration of the ion-exchange bed presents further not negligible expense, which increases the final product costs.

The electrodialysis has a potential to be an alternative method for the colloidal silica manufacturing. Even though the efforts of colloidal silica production with electrodialysis are known for several years, they are still in recent researcher

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interests [7,8], because of the fact that the experiment reproducibility with different electrodialysis devices and membranes are not comparable and experimental conditions then have to be properly adjusted to fit certain approaches with available equipment.

Here we describe our method for the preparation of silica solution suitable for the concentration by the electrodialysis, which involves pH alteration with weak acid. The novelty in our procedure is the utilization of phosphoric(V) acid, which evinces simple initial solution's pH alteration and enables further total removal of phosphoric ions by electrodialysis. Nucleation and following concentration of colloidal silica then takes place in electrodialysis unit equipped with commercially available RALEX® membranes. The overall mechanism and process control of the concentration step is here described and explained. According to our knowledge, our method is economically acceptable and offers the possibility of replacing the current production by ion-exchange columns.

2. Equipment

Electrodialysis (ED) was performed on an electrodialysis unit P EDR-Z/10-0.8 Type 13, from MemBrain Company [9,10]. During the ED process, ions are transported through semi-permeable membranes (RALEX®, MEGA a.s. [11]) under the influence of applied electric potential. The main core of this apparatus represents a membrane stack, which consists of 10 planar-plate anion-exchange membranes (AM) and 11 planar-plate cation-exchange membranes (CM), which are alternately ordered in the stack. This set-up enables either positive ions and/or negative ions removal from a solution. Individual membranes are separated by inert (electrically non-conducting) mesh-like spacers, providing mainly a mechanical support of the stack and determining the geometry of the flow channel creating overall 20 chambers of thickness 0.8 mm as the space between stacked membrane pairs. Two independent hydraulic circuits were employed: diluate (D) and concentrate streams (C) supplied with solutions from the diluate tank and concentrate tank, filled by 1 L of the pretreated sodium silicate (concentration 3% w/w) and 1 L of Na_2SO_4 20 g/L, respectively. The membrane stack was placed between two terminal planar-plate electrodes, which compartments were also fed by 200 mL solution of Na_2SO_4 20 g/L that was circulated in closed independent loop. Flow rate for each circuit (diluate, concentrate and electrolyte) was set to 50 L/h.

Voltage applied on the membrane stack was 1.2 V/pair. Sodium ions are transferred from diluate (solution of diluted sodium silicate) through the cation exchange membranes to concentrate stream during the electrodialysis process. OH^- ions are transferred from the diluate through anion exchange membranes to the concentrate stream to ensure the charge balance. Temporarily present silicic ions are not transferred and thus solid SiO_2 particles could be formed. The process is schematically indicated in Fig. 1. Such set-up was used during all electrodialysis experiments.

3. Experiments

The whole procedure was separated into two steps: (I) nucleation and growth, and (II) concentration. Our starting solution was 40% w/w sodium silicate with ratio SiO_2/Na_2O = 3.4 and pH 11, which has to be modified before being poured in the electrodialysis diluate tank. The starting solution must be diluted to decrease its viscosity and increase solution's stability during following acidification. Without pH adjustment, it is possible to process the solution only in certain concentration limits according to the ternary phase diagram (Fig. 2).

Diluted solution's pH must be decreased to ensure that the following electrodialysis would not transfer silicate ions to the concentrate stream and the formation of colloidal particles will be initiated. It was observed that only small amount of diluted acid has to be continuously dosed to the solution to reach the demanded decreased pH in range of 8 to 9. Higher dose of acid produces gel of silicic acid even at high dilution ratio. It was observed that the sodium silicate solution below pH 8 can be also reached; however, the long-term stability of the solution is then significantly shortened

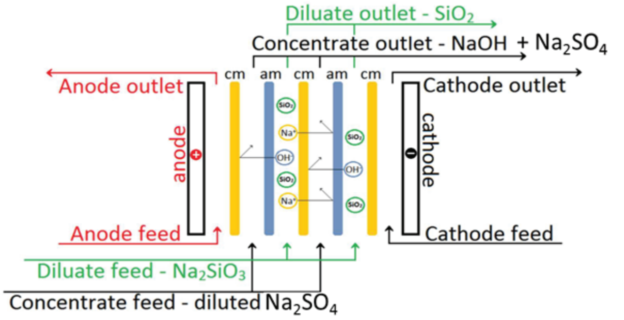

Fig. 1. Schematic of phenomena during electrodialysis of sodium silicate solution.

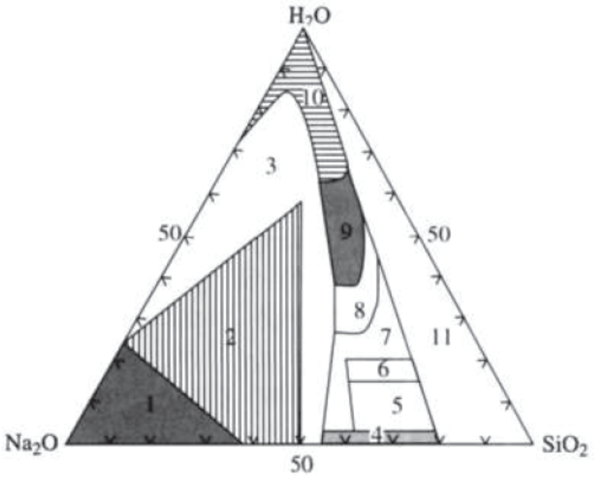

Fig. 2. Ternary phase diagram of the system Na_2O-SiO_2-H_2O. Areas: (1) anhydrous Na_4SiO_4 and its granular mixtures with NaOH, (2) granular crystalline alkaline silicates and their hydrates, (3) partially crystallized mixtures, (4) glasses, (5) hydrated glasses, (6) dehydrated liquids, (7) semi-solids and gels, (8) unstable viscous liquids, (9) ordinary liquids, (10) dilute liquids and (11) unstable liquids and gels. Taken from a study by Vail [12].

(stable only for several hours). Suitable concentration of the starting solution for electrodialysis processing ranges from 1% to 3% w/w. Several samples of the starting solution using different acids were tried to prepare. Our results are summarized in Table 1.

Sample d from Table 1 was considered as the most suitable from the stability and initial highest concentration points of view and thus was used for all further electrodialysis experiments.

I) Nucleation and growth step was carried in the electrodialyser, where sodium ions and phosphate ions, added during acidification, are removed. Process was controlled by continuous decrease of solution's conductivity in the diluate stream. The starting conductivity of the initial (2% w/w) solution was 10 mS/cm. The electrodialysis process continued until the conductivity in the diluate stream reached value 1.41 mS/cm, which corresponds to commercial colloid silica sample diluted to 2% w/w. Nucleation and growth step electrodialysis set-up is summarized in following points:

- Diluate feed: 2% w/w sodium silicate
- Concentrate and electrolyte feed: Na_2SO_4 20 g/L
- Flow rate (all circuits): 50 L/h
- Membranes: 10 pairs (CM-AM-CM – stack)
- Voltage: 1.2 V/pair
- End conditions: diluate conductivity 1.4 mS/cm

II) The concentration steps were carried out immediately after the first step finishes. A small amount of 40% w/w solution of sodium silicate was dosed to the mixed diluate tank. Each addition of the 40% w/w solution also continuously increases the pH in the diluate, thus further addition of the acid is necessary to ensure that the pH do not overcome value 10.5, because, as mentioned above, higher pH allows unwanted transfer of silicate ions to the concentrate stream. This phenomenon is assigned to the polarization of the surface of colloid particles to the negative one, which enables migration in the electric field and transfer to the anion exchange membrane surface, where could cause a clogging [13]. The dosing of the phosphoric acid must be precisely controlled, while overdosing to pH lower than 7.0 would cause gelation of the solution. This was also confirmed by observation of study of Brown [14] where was estimated that maximal solubility of amorphous silica at pH 7 and 25°C is 120 ppm. Addition of fresh sodium silicate together with continuous sodium and phosphate ions removal increases concentration of the silicic acid in the solution with nuclei and so the concentration and the partial growth take place. While ions are continuously removed by electrodialysis, the conductivity in the diluate decreases. When the conductivity decreases to the value that corresponds to particular concentration of the commercial sample, then new fresh dose of silicate was added. Whole procedure was repeated until a 10% w/w concentration of the solution in the diluate stream was reached.

Table 1
Stability of prepared solutions

Sample	Solution concentration (w/w)	pH	Acid concentration	Result
a	1%	8.5	H_2SO_4 1%	Gel
b	1%	9.0	H_3PO_4 1%	Stable
c	1%	8.5	H_3PO_4 2%	Stable
d	2%	9.0	H_3PO_4 2%	Stable
e	2%	8.5	H_3PO_4 2%	Gel

4. Results and discussion

The progress of the first step evinces moderately linear decrease of the conductivity in the diluate stream, which confirms almost constant transfer rate of ions through membranes. This transfer rate slightly decreases at lower ion concentration in the diluate stream at the end of the step. According to datasheet taken from the manufacturer of the RALEX® membranes, the desalination of Na_2SiO_3 is almost four times slower than similar tests carried with proper concentration of Na_2SO_4. It is assumed that formation of colloidal particles together with continuous increase of SiO_2 concentration prevent the sodium ions transfer by shielding them in the solution. The same effect is also observable during the second step. The progress of both steps is summarized in Fig. 3.

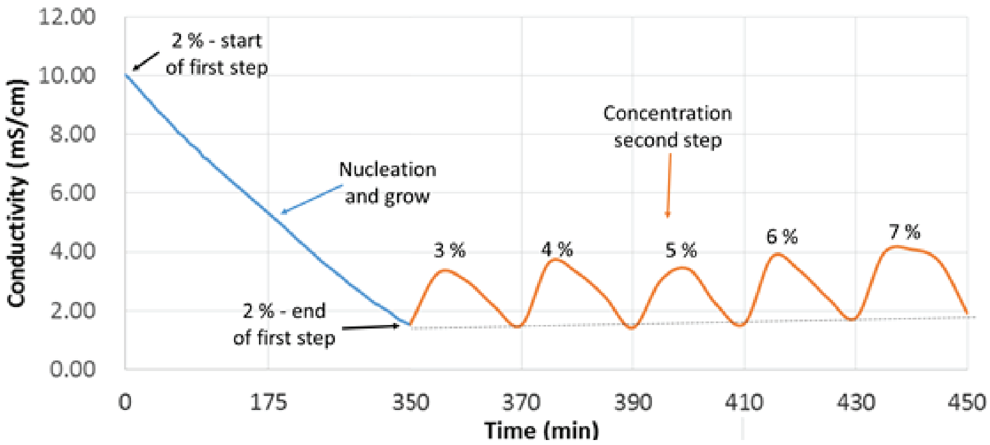

Fig. 3. Electrodialysis – conductivity progress for first and second step in the diluate stream.

Each addition of the fresh (40% w/w) sodium silicate becomes evident as a step (increase of the conductivity) followed by the conductivity decrease while ions are removed. The concentration time slightly increases after each addition because of the increasing concentration of colloidal particles followed by the increasing effect of ions shielding. The slow sodium transfer from the solution above 10% w/w concentration is economically unacceptable. It is also obvious that ending conductivity for each following concentration degree slightly increases because of the increasing content of remaining sodium ions. This trend has to be maintained to ensure that the increasing concentration of the colloidal silica in the solution will be stable. Gelation occurs without enough sodium ions presented in the concentrated solution. The deformation of conductivity peaks is caused by addition of phosphoric(V) acid if necessary for maintaining pH in certain limits above 8.0 and below 10.0 (Fig. 4).

In every additional concentrated percentage, a sample was taken and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES – iCAP 7000 Series) to verify that sodium was removed and silicon was concentrated as expected. The analysis results are summarized in Table 2.

It can be noticed that the sodium concentration at the beginning of the process (2% start) was high and greatly diminished when the conductivity reached the minimum, while silicon concentration remained constant. The small difference between the two quantifications may have happened because of OH^- transfer, thus reducing the volume in the diluate stream and increasing the concentration progress. The more amount of fresh sodium silicate was added, the higher the concentration of the silicon was reached.

To confirm that the produced colloidal silica evinces a good quality, particle size distribution was measured on a Zetasizer Nano ZS, from Malvern Instruments Ltd. (UK) (Fig. 5). Measurements confirmed that the produced 10% w/w solution has a very narrow distribution with particles size 8 ± 2 nm. As previously quoted at the introduction section, SiO_2 with particle size below 10 nm is considered as a high quality colloidal silica, so the produced solution meets the quality requirements.

With respect to simulations obtained from CurTiPot [15] silica overall charge is neutral in solutions below pH 8.0 and so they are not influenced by electric current during electrodialysis. Increase of pH causes induction of negative charge on silica molecules –1 at pH above 10.5 up to –2 at pH 14.0 (Fig. 6(a)). Polarization of silica molecules is not desired in our experiments because charged silica molecules are transferred to anion exchange membrane surfaces where causes clogging of the membranes by gelation due to the higher local concentration of the silica. Obtained CurTiPot simulations are also in good agreement with theory of the colloidal particles formation from the sodium silicate solution at certain pH (Fig. 6(b)).

Laboratory experiments and field observations have shown that there are a number of factors that affect the kinetics of silica deposition. Some of the more important are: (1) degree of supersaturation, (2) pH, (3) temperature, (4) flow rates,

Table 2
Sodium and silicon concentration (w/w) analysis in diluate stream

Sample	Result (mg/L)		
	Na	Si	SiO_2:Na_2O
40% sodium silicate	75,635	176,341	3.05
2% start of first step	3,240	7,600	2.35
2% end of first step	444	7,760	17.48
3%	499	10,200	20.44
4%	426	13,200	30.99
5%	617	16,200	26.26
6%	632	20,100	31.80
7%	660	22,300	33.79

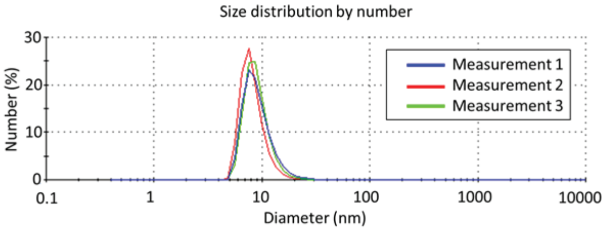

Fig. 5. Particle size distribution of 10% w/w solution.

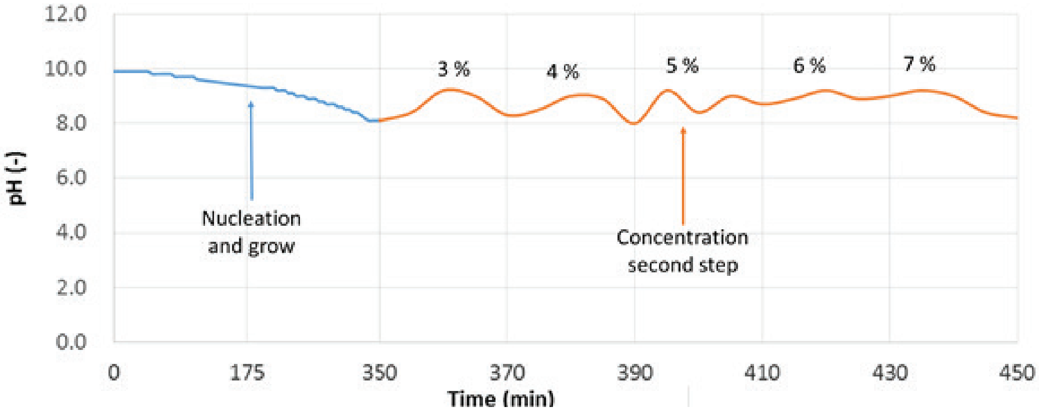

Fig. 4. Electrodialysis – pH progress for first and second step in the diluate stream.

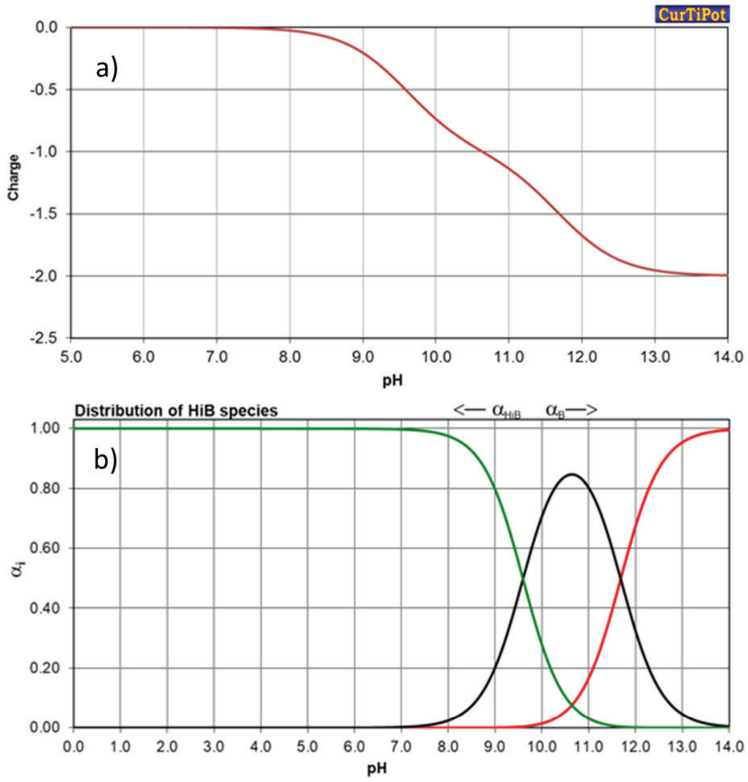

Fig. 6. CurTiPot simulation of charge induction on silica (H_2SiO_3) molecules at different pH values (a) and simulation of silica ionic forms, green H_2SiO_3, black ($HSiO_3^-$) and red (SiO_3^{2-}) at different pH values (b). HiB stands for proton (H^+) in base and α_i express concentration fraction of *i*th silica ionic form.

(5) aeration, (6) other ions in solution. In general, the deposition of amorphous silica follows one of two possible mechanisms: (I) the preliminary formation of a colloid and its subsequent precipitation. (II) Direct deposition onto solid surfaces.

Ion-exchange columns typically produce silica sol of concentrations 3.5%–4.5% w/w and the final concentration (up to 40% w/w) is reached with use of an evaporator. Evaporator energetic demands are assumed 0.05 kWh per liter of distillate. 4 L of diluted silica sol (3.5% w/w) then consumes 0.1 kWh in order to increase initial concentration two times.

The comparison colloidal silica that has concentration up to 10% w/w was able to be produced. According to our experiments, where 4 liters of diluted sodium silicate has been processed, the first step consumes approximately 33.1 Wh and second step which was stopped at final concentration 7% w/w consumes approximately 4.8 Wh (energy consumed by pumps is not considered in these calculations). With respect to these energy balances it is obvious that electrodialysis is almost 2.6× less energy demanding than the evaporator in the case of production of 7% w/w silica sol.

5. Conclusion

Fine colloidal solution of 10% w/w silicon dioxide was successfully manufactured with utilization of the electrodialysis unit equipped with RALEX® membranes. We suggested preparation of initial solution for subsequent electrodialysis process with use of diluted phosphoric(V) acid. It was found that suitable conditions based on pH control and proper sodium silicate dosing, which ensure the long-term stability of the continuously concentrated solution. Keeping the solution's stability during the concentration step is the crucial attribute from the electrodialysis proper function point of view. High production quality and low energy demands give electrodialysis enormous potential to replace the standard technology based on ion-exchange columns and evaporator. The main drawback of the electrodialysis silica sol production is that further concentration above 10% w/w significantly increases operational costs and overall production time. Deeper investigation of phenomena, which arise at higher silica sol concentration, must be carried out to enable further effective operation of the electrodialysis unit. Obtained sol could be provisionally more concentrated with other membrane techniques, for example, ultrafiltration, however increasing concentration that shifts the stability equilibrium must be then taken into consideration. In case of the industrial production, every concentration degree that is reached before the final evaporation noticeably decreases operational costs of the evaporator.

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