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Separation of medical nanopowder from the natural minerals by supercritical CO_2

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Abstract: Nano-sized medical raw material has been derived from the medical quality natural spar ($CaCO_3$) without the use of chemical salt. The theoretical base of the method consists in the transferring and keeping CO_2 to a supercritical state during thermo-chemical processing of the spar at 900-950°C. The supercritical CO_2 has a form of solid solution that holds the properties of both gas and solid. Afterwards, with dissolving it in the animal milk, the solution is equalized by the sovent's expansion with the decrease of temperature and creates amorphous crystal nanopowder. The size of the resultant product was determined both by XRD and TEM analysis as to be 13.51 nm (Lu »13.09 nm).

Keywords: Supercritical CO_2, saturated gas, nanopowder, spar, amorphous crystal

INTRODUCTION

Carbon dioxide exists as a gas, as a liquid and as a solid called dry ice when frozen. Above its critical temperature and pressure, it behaves like a supercritical fluid with unique properties of both gas and liquid. Such CO_2 has the ability to diffuse through solids like a gas and dissolve materials like a liquid. Besides, it can readily change in density upon minor changes in temperature and pressure. All these properties make it suitable for use as organic solvents. The critical point of a substance was first discovered by Charles Cagniard de la Tour in 1822 and named by Andrews in 1869. With the increase of pressure, density increases and it is possible to change pressure and increase solubility [1-3]. Since 1991 the supercritical CO_2 ($ScCO_2$) have been studied extensively in various experiments such as nanopowder extraction and increase of cement's quality in the laboratories of different countries. However, the interaction of the material by $ScCO_2$ requires specific devices with complicated construction, which makes the process cost ineffective [1-5]. The traditional methods, we experimented, have unique advantages keeping $ScCO_2$ in the primary material by simple, cost-effective and high productive way, avoiding necessity of grinding a material to a smaller particles, of using chemical salts. It is green, ecologically pure, ready to use for industrial production [6, 7]. By this article, I aimed to prove that our experiment made on the basis of the traditional technology is performed at the current nanotechnological level and to explain its scientific substantiation by modern scientific expressions.

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The easiness wonders one, but if based on the great Mongolian traditional knowledge, the great can be created by the simplest way. As it is well documented, Mongolians (between XIII and mid of XX centuries) were famous in Asia and Europe by preparing drugs against any kind of diseases from medical minerals in combination with plant or animal origin materials. In drugs source manuscript [8] noticed about hermetic burning and taming of spar and utilization it after enhancing/nutriting (synthesizing or processing) by animal milk, yogurt or fat. In [9] it is defined the hermetic burning of spar removes organic toxic mixtures but keeps the composition as it is. Among them is flammable carbon dioxide CO_2, which does not volatilize but remains in the spar. Importance of CO_2 as it dissolves minerals and transfers energy in the drugs were documented in [7, 11]. During the synthesizing of tamed spar with milk, spar turns into the nano-sized powder without addition of any other substances. This fact has proved our explanation and that CO_2 is a good solvent [7, 9]. As noticed in the manuscript [8] our ancestors were processing it during three hours on the cattle droppings fire. We have processed it in a less than three hours and extracted medical nanopowder (13.51 nm) for the first time [11-12]. The spar tamed by such a method had been used for preparing drugs against coronary diseases, gastritis, esophageal cancer, brain damage and osteoporosis [6-12].

EXPERIMENTAL

For our experiment we have used about 30 kinds of mineral samples collected from the Gobi region of Mongolia.

The used equipments for the thermo-chemical processing are the iron pot (Æ~12 cm, height≈8 cm) with hermetic tap and the muffle furnace (1000°C). The preparation of the natural spar for the processing was implemented as described in [9]. The analyses were carried out by modern chemical, physical-chemical and mineralogical equipments. These are:

- X-ray and chemical silicate analysis for chemical composition determination of natural minerals and technological products
- Complete chemical silicate analysis, AAS-3, ICP-OES, X-ray fluorescence, atom emission spectrum
- Chemical, physical, IR spectral, refractometer and microscopic methods (TEM) for determination of technological product's composition, size and chemical bonds.

Experimental procedures: The process of separation of medical nanopowder from the natural minerals has been described in detail in our previous studies [6, 7, 9, 10-12]. Therefore, here we briefly outline that the process comprises main two steps, namely: 1) decomposition of medical minerals by only thermal method without the use of chemical salts, removing toxic substances and keeping the CO_2 in the primary material; 2) enhancing/nutriting by plant or animal origin solvents. The flowchart of the process is shown in Fig.1.

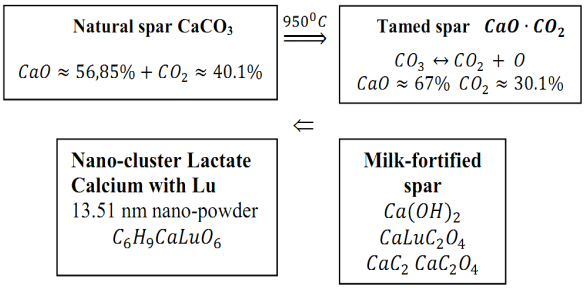

Fig. 1. Flowchart of the process

We selected the Iceland spar to decompose by thermo-chemical method keeping its primary weight at the temperature above 950°C. The process of spar decomposition can be written as:

$$CaCO_3 \xrightarrow{t^0C} CaO \cdot CO_2 + Q \qquad (1)$$
$$CO_3 \leftrightarrow CO_2 + O$$

As seen from the equation (1), by the thermo-chemical processing of the spar, the carbonate calcium spar ($CaCO_3$) of hexagonal structure decomposes and turns into the calcium oxide (CaO) of cubic structure. In addition, carbon dioxide (CO_2) does not evaporate but is adsorbed into calcium oxide, which was determined by the main element content (CaO and CO_2) in the product of burning. Thus, two-phase solid solution is created due to the $ScCO_2$ (gas saturation solution).

The resultant CO_2 has an important role to transfer energy to organism cells improving metabolism and CaO solubility. $ScCO_2$ is a solid substance and serves as an important solvent for transferring any kind of solid, liquid solutions into amorphous crystal form. Therefore, in the world practice, in order to derive medical nanopowder $ScCO_2$ is usually added to the target material either in gas or liquid form. In contrast to this, in the Mongolian traditional technology the thermal processing of medical material does not loose CO_2 but keeps it in the target material. This fact distinguishes our traditional technology from the current modern technology by easiness and cost effectiveness. By the processing of the solid liquid with cow milk, temperature decreases, solution is equalized and an amorphous nanopowder is created in the result of the expansion of the organic solvent. The main factor influencing on the production output is the concentration of the supercritical liquid and it depends on the proportion of the primary solution. The output of the nanopowder and rate of the crystallization depend on temperature decrease and supercritical liquid amount.

Working temperature and pressure transform to the atmospheric condition as a solution expands. With the temperature decrease by the influence of the CO_2 solvent, equalization is established in the solution until it rich the normal condition. CO_2 serves as solvent in the process of solution crystallization. Small particles are created by the influence of saturated solution of gas and process of separation takes place. The process of crystallization depends on temperature decrease and output is determined by the amount of total supercritical fluid. Powder has a circle form.

RESULTS AND DISCUSSION

The compositional analysis of the spar, enhanced/ nutrited by cow's milk, is performed by the X-ray fluorescence and its purity and the characteristics of the created metal-organic bond are shown in Fig. 2 and 3, respectively. The infrared (IR) spectral analysis of its bond structure (Fig.5) shows that after nutriting by milk (milk-fortified) acids the active ligands (COO^-, C-H, C-C, O-H, COOH) are formed that are able to create a metal-organic composition. Tables 1 and 2 show the chemical composition of the tamed spar. The electron microscope analysis determined the purity of the tamed and milk-fortified spar as to be of 98% $Ca(OH)_2$ with the size of 10^{-11} - 10^{-9}m. It is seen that its Ca creates with lanthanum group elements such compounds as calcium-lutetium oxalate ($CaLuC_2O_4$) of lactic acid, calcium oxalate (CaC_2O_4), calcium carbide (CaC_2) (Fig. 2).

Table 1. Main compounds (%) of newly derived raw medical material defined by x-ray fluorescence method

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	CO_2, C_{org}, H_2O, etc
0.12	<0.001	<0.003	0.04	0.002	0.29	67.57	<0.005	0.022	0.12	30.41

Table 2. Microelements content, mg/kg

F	∑	As	Ba	Ce	Co	Cs	Cu	Ga
<0.05	98.50	<	<5	<20	<5	<25	11	<3
Hf	La	Mo	Nb	Nd	Pr	Pb	Ni	Lu
<15	<30	<5	<3	<50	<30	<5	<5	<30

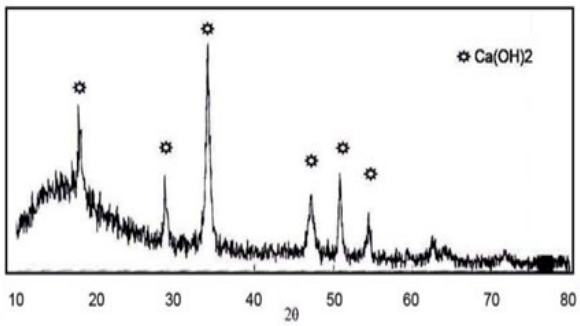

Fig. 2. Calcium hydroxide content in the nutrited spar (98% purity)

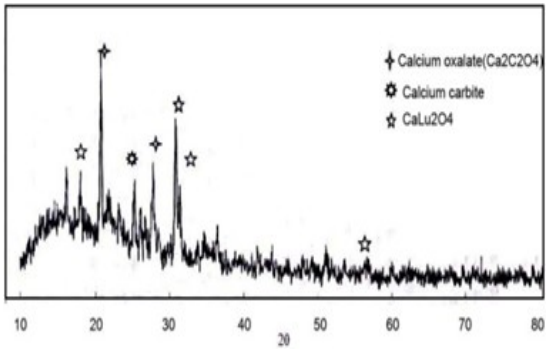

Fig. 3. Characteristics of metal-organic bond in the structure of the tamed spar

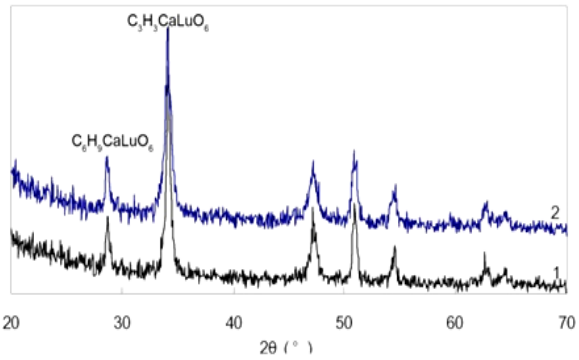

Fig. 4. Sample analysis by X-ray diffractometer

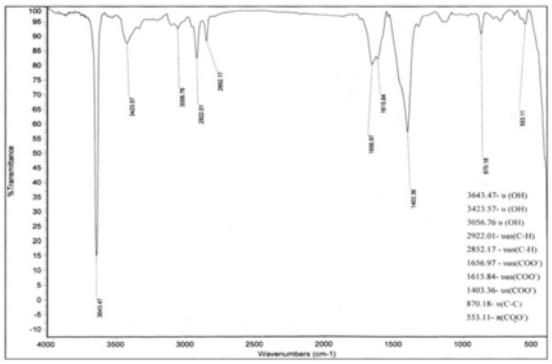

Fig. 5. IR spectrum of enhanced/nutrited spar

X-ray diffraction patterns of the spar show $C_6H_9LuO_6$ peak at refraction index of 2θ=20.719, $C_3H_3LuO_6$ peak in P350969 card at the refraction index of 2θ=34.011 (Fig. 4) suggesting that Lu connected with the lactate calcium in the lactic acid environment. Hydrate peaks are revealed at 2θ=47.212, 50.960, 54.462, 62.623, 64.450 respectively.

Based on the X-ray diffractometer's analysis we calculated the diffraction peak using Bragg's equation and the size of Lu to be 13.09 nm and 13.51 nm for $C_6H_9CaLuO_6$ using Scherrer equation (Eq. 2):

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos\theta} \qquad (2)$$

Where: D is the crystallite size, l is the diffraction wavelength, b is the full width at half maximum (FWHM) of a diffraction peak, q is the diffraction angle and K is a constant close to unity.

The last products of few experiments we have carried out were analyzed by high-resolution TEM in the Nanotechnological Laboratories of Inner Mongolia University of Technology, which revealed the size is reduced till 5 nm (Fig.6).

Light adsorption of humic substances is higher, based on double bond (C=C and C=O) in molecular structure of humic substances. Adsorption measurement depended on content of polar functional group in sample. Light adsorption of samples in the UV-Vis region, a decrease on the absorption intensity with an increase of the wave length was observed (Fig. 2). The analysis of spectrum showed that humic substances isolated from peloid and coal presents a weak intensity at the field of 274 - 277 nm in ultra-violet and vizible region, attributed to the ionization phenolic hydroxyl groups (or only aromatic structures).

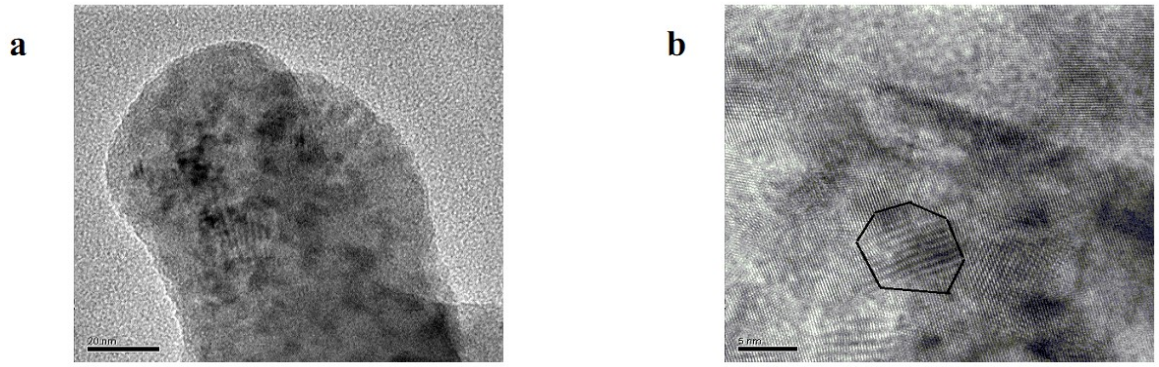

Fig. 6. The high resolution TEM images of ($C_3H_3CaLuO_6$) samples. The left image (a) is the CaO amorphous nanopowder keeping $ScCO_2$ (at 950°C). The right part (b) shows a detail at higher magnification with clearly observable crystallites that were created in the result of enhancing/nutriting (a) by milk, after its temperature decrease.

The TEM pictures were captured by a high resolution TEM (HRTEM) JEM 2010 with a capability to resolve lattice spacings of approximately 0.14 nm and point resolution of 0.23 nm. As seen from the morphology of the nanoparticles, these samples are assembled by randomly oriented spherical nano-crystallites. Fig. 6b shows more crystallites, which is in accordance with the XRD results.

This analysis also confirms that lanthanides create with lactic acid the complex compound (co-ferment) of the $CaLn(CH_3CHOHCOO)_3$ form, and Ca and Lu bond with lactic acid by oxygen.

CONCLUSIONS

1. High resolution TEM image (Fig. 6) proved that in the result of the thermo-chemical processing of the natural spar are created: (a) amorphous powder CaO (»20nm) keeping $ScCO_2$ (at 950°C); (b) crystallite powder (»5nm) in the result of the organic solvent's expansion.
2. In addition, the size of the created lactate calcium -lutetium ($C_3H_3CaLuO_6$) is calculated using diffraction peak of the X-ray analysis of the crystallite powder according to Bragg's equation and consequently Scherer formula as to be 13.51 nm (Lu »13.09 nm).
3. The metals Ca and Lu are connected with ligands (COO, C-C, C-H, COOH, OH) and create the metal-organic (co-ferment) compounds ($C_6H_9CaLuO_6$ and $C_3H_3CaLuO_6$) which is revealed by X-ray diffractometer analysis.
4. The advantages of supercritical CO_2 method are easiness, cost effectiveness and high productivity. The output is ecologically clean nanopowder suitable for utilization not only in the traditional drug preparation field (it is served as raw material for preparation of such drugs as gurgem-9, golotag-tug, shijid, dejidnyamdan) but also it can be used in food supplementary and cosmetics preparation fields [11-12].

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