

Separation of Medical Nanopowder from the Natural Minerals by Supercritical CO₂

J.Oyun

Chemistry Department, Ulaanbaatar University, Ulaanbaatar, Mongolia.

Received: March 31, 2015 / Accepted: April 29, 2015 / Published: July 25, 2015

Abstract: Nano-sized medical raw material has been derived from the medical quality natural spar (CaCO₃) without the use of chemical salt. The theoretical basis of the method consists in the transferring and keeping CO₂ to a supercritical state during thermo-chemical processing of the spar at 900-950°C. The supercritical CO₂ 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 solvent's expansion with the decrease of temperature and creates amorphous crystal nanopowder. The size of the resultant product determined by both factors.

Keywords: Supercritical CO₂, saturated gas, nanopowder, spar, amorphous crystal.

1. 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 CO₂ 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 CO₂ (ScCO₂) 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 ScCO₂ requires specific devices with complicated construction, which makes the process cost ineffective [1-5]. The traditional methods, we experimented, have unique advantages keeping ScCO₂ 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. The easiness wonders one, but if based on the great Mongolian traditional knowledge, the great can

Corresponding author:

J.Oyun, Chemistry Department, Ulaanbaatar University, Ulaanbaatar, Mongolia. E-mail: jambaoyuna@yahoo.com.

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, 13-18] 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 CO₂, which does not volatilize but remains in the spar. Importance of CO₂ 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 CO₂ 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].

2. Materials and Methods

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 (Ø~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 CO₂ in the primary material; 2) enhancing/nutriting by plant or animal origin solvents. The flowchart of the process is shown in Fig.1:

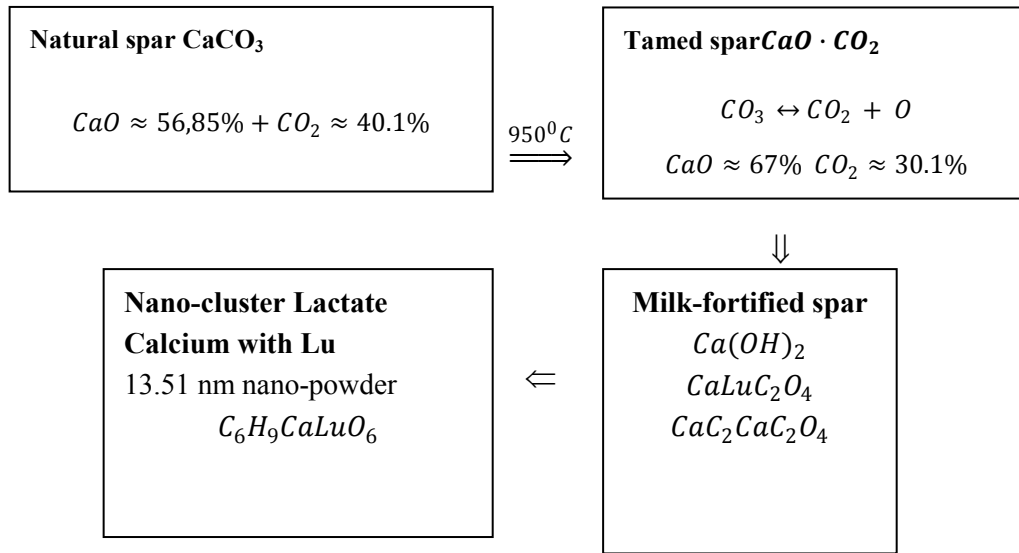


Fig. 1 Flowchart of the process

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:



As seen from the equation (1), by the thermo-chemical processing of the spar, the carbonate calcium spar (CaCO₃) of hexagonal structure decomposes and turns into the calcium oxide (CaO) of cubic structure. In addition, carbon dioxide (CO₂) does not evaporate but is adsorbed into calcium oxide, which was determined by the main element content (CaO and CO₂) in the product of burning. Thus, two-phase solid solution is created due to the ScCO₂ (gas saturation solution). The resultant CO₂ has an important role to transfer energy to organism cells improving metabolism and CaO solubility. ScCO₂ 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 ScCO₂ 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 CO₂ 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 CO₂ solvent, equalization is established in the solution until it rich

the normal condition. CO₂ 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.

3. 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 (CaLuC₂O₄) of lactic acid, calcium oxalate (CaC₂O₄), calcium carbide (CaC₂) (Fig. 2).

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

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂ , C ₁₀₀ , I ₂ I, 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

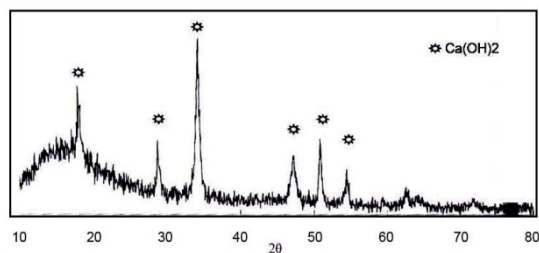


Fig. 2. Calcium hydroxide content in the nutrified spar (98% purity)

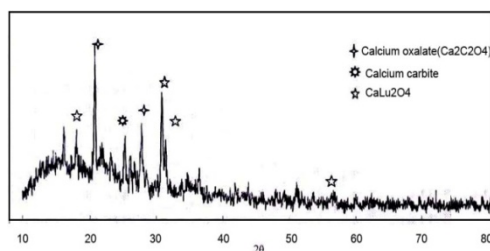


Fig. 3. Characteristics of metal-organic bond in the structure of the tamed spar

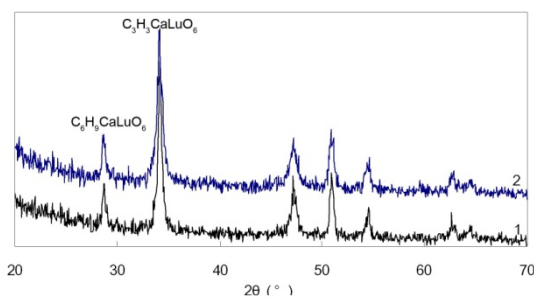


Fig. 4. Sample analysis by X-ray diffractometer

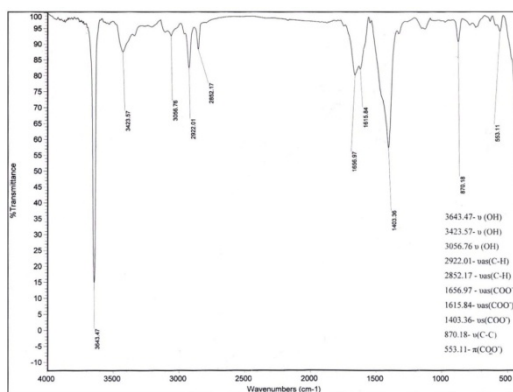


Fig. 5. IR spectrum of enhanced/nutrified spar

X-ray diffraction patterns of the spar show C₆H₉LuO₆ peak at refraction index of $2\theta=20.719$, C₃H₃LuO₆ peak in P350969 card at the refraction index of $2\theta = 34.011$ (Fig. 4) suggesting that Lu connected with the lactate calcium in the lactic acid environment. Hydrate peaks are revealed at $2\theta = 47.212, 50.960, 54.462, 62.623, 64.450$ 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 C₆H₉CaLuO₆ using Scherrer equation (Eq. 2):

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

where D is the crystallite size, λ is the diffraction wavelength, β is the full width at half maximum (FWHM) of a diffraction peak, θ is the diffraction angle and K is a constant close to unity. The last product 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). The TEM pictures were captured by a high resolution TEM (HRTEM) with an ability to magnify 500000. As seen from the morphology of the nanoparticles, these samples are assembled by randomly oriented spherical nano-crystallites. Fig. 6b shows more crystallinity, which is in an accordance with the XRD results.

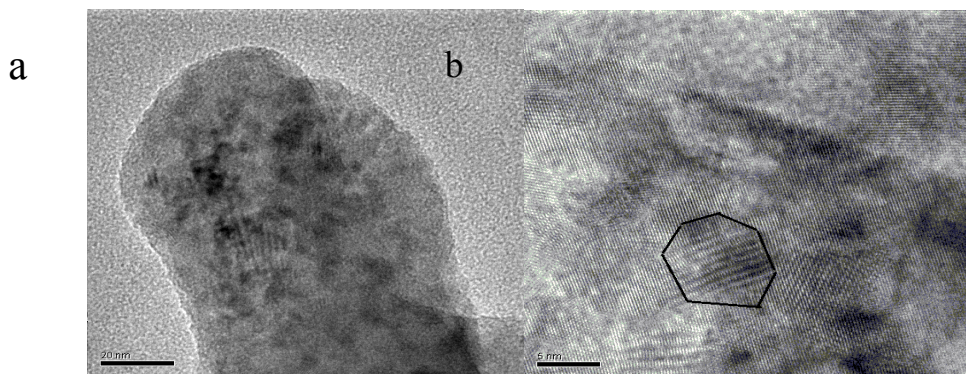


Fig. 6. TEM images of (C₃H₃CaLuO₆) samples (HRTEM, 500.000x mag). The left image (a) is the CaO amorphous nanopowder keeping ScCO₂ (at 950°C). The right part (b) shows a detail at higher magnification with clearly observable crystallites that were created in the result of enhancing/nutriting (a) by milk, after its temperature decrease.

This analysis also confirms that lanthanides create with lactic acid the complex compound (co-ferment) of the CaLn(CH₃CHOHCOO)₃ form, and Ca and Lu bond with lactic acid by oxygen.

4. Conclusion

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 (≈ 20 nm) keeping ScCO₂ (at 950°C); (b) crystallite powder (≈ 5 nm) in the result of the organic solvent's expansion.

2. In addition, the size of the created lactate calcium-lutetium (C₃H₃CaLuO₆) 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 (C₆H₉CaLuO₆ and C₃H₃CaLuO₆) which is revealed by X-ray diffractometer analysis.
4. The advantages of supercritical CO₂ 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].

Acknowledgments

The author expresses sincere gratitude to N. Ulzijargal (Ph.D.) for her effort in determining the nanosize of the tamed spar by the TEM in the Nanotechnological Laboratories of Inner Mongolia University of Technology. The author would like to thank the reviewers for their comments that help to improve this paper.

References

- [1]. Changlei, Q., Junjun, Y., Cong, L., Hui, A., Wenqiang, L., and Feng, B. (2013). Enhancing the performance of CaO/CuO based composite for CO₂ capture in a combined Ca-Cu chemical looping process. *Chemical Engineering Journal*.228, pp. 75-86.
- [2]. Dunkley, R. (2004) *Nanotechnology: social consequences and future implications*. Future.
- [3]. Subra, P., Berroy, P., Vega, A., and Domingo, C. (2004) Process performances and characteristics of powders produced using supercritical CO₂ as solvent and antisolvent. *Powder technology*. 142, No.1, pp.13-22.
- [4]. Reverchon, E., and Antonacci, A. (2007) Polymer microparticles production by supercritical assisted atomization. *J. Supercrit. Fluids*. 39, No.3, pp.444-452.
- [5]. Zalepugin, D. Yu., Til'kunova, N. A., and Chernysheva, I. V., Polyakov, B. S. (2006) *Supercritical fluids: theory and practices*. 1, No.1, pp.5-23 (in Russian).
- [6]. Oyun, J. (2006) *Physical and chemical technological studies of medical minerals of Mongolia*. Ulaanbaatar, pp. 430, ISBN 09929-0-488 (in Mongolian).
- [7]. Oyun, J. (2006) *Theoretical-methodological analytical studies of enrichment of the rare earth elements in the mineral by polymer reagents*. Ulaanbaatar, pp.154. ISBN 99929-6-355-7. (in Mongolian).
- [8]. Ishbaljir. (XYII century) *Crystal mirror for recognition of name and medical minerals*. Mineral drugs. XYII century, pp. 1704-1810 (in Mongolian).
- [9]. Oyun, J. (2002) *Physical-chemical investigation of medical quality minerals of Mongolia, and scientific substantiation of their taming methodology*. Sci. Dissertation. pp. 369. Ulaanbaatar.

- [10]. Oyun, J., Tserenkhuu, Ch., and Munkhjargal, Sh. (2009), Chemical-biological studies of rare earth's elements in the medical minerals of Mongolia. Proceedings of the 10th Asian Conference on Analytical Sciences, pp. 85. 13 August 2009. Kuala Lumpur, Malaysia.
- [11]. Oyun, J. (2007), Studies of origin of medical minerals of Mongolia. Proceedings of the 9th Asian Conference on Analytical Sciences, pp.137. August 2007. Jeju, Korea.
- [12]. Oyun, J. (2009), Study of natural medicinal quality minerals and plants: their use as nutrition's complement. The first International Symposium on chemistry of Herbal medicine and Mongolian drug. July 2009. Hoh hot.
- [13]. Danzanvaanchig, Gegeen khumrug, XVIII century (in Mongolian).
- [14]. Chud-shii, Memorial of middle century, Tibetan medicine, Russian translation, Novosibirsk, 1988, "Nauka" pp100.
- [15]. Luvsanchultem, Science of recognition of medical gemstones, soil and rocks, XVIII century, Tibetan manuscript.
- [16]. Ishbaljir, Crystal mirror for recognition of name and medical minerals, 1708-1810.
- [17]. Ishdanzanvaanjil (1874-1907), Jurdushil, XIX century, Ordos, Inner Mongolia.
- [18]. Ishbaljir (1704-1788), Anagaakh shinjlehuin rarshaany dusal, XVIII century (in Mongolian).