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APPLICATION PERSPECTIVES OF THE AVAN SALT MINE'S BOTTOM SEDIMENT'S HIGHLY MINERALIZED CLAY IN MEDICINAL CLAYS AND COSMETOLOGY

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Abstract

The healing and cosmetological properties of clays have been known since ancient times. The clay's healing and cosmetic properties are used to treat various diseases and have

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medicinal uses for skin quality improvement. The objective of this paper is to study the quantitative composition of highly mineralized clay, which is a bottom sediment separated during the processing of the raw material extracted from Yerevan Avan Salt Mine, and to identify the possibilities and scope of its application. The formulation of healing clays, anti-inflammatory agents, pain-relieving balms, beauty products, and skin scrubs having improved properties was developed using stable combinations of highly mineralized clay and natural additives based on the experimental findings.

Key words: rock salt, mineralized clay, microelements, propolis, anti-inflammatory agent.

Introduction

Clay is a universal remedy for strengthening the immune system and treating various diseases, such as arthritis and polyarthritis, spinal diseases of non-tuberculosis origin, inflammatory and post-traumatic diseases of bones, muscles, and tendons, digestive system diseases, and diseases of female genital organs. Clay is used in creams, pastes, rubbings, healing baths, aqueous suspensions, triturations, applied to painful points, etc. However, a scientifically based assessment of the healing properties of clay is not yet sufficient. More research is needed before scientists will know the true benefits and risks of clay in humans. It is known that all clays have one unique property: they absorb toxins. Therefore, clay, if used wisely, cannot be harmful or risky. Each group of clay, depending on the impurities included in the composition, has its own function and use [1]. Analyses have shown that clay contains high quantities of mineral salts and trace elements, which are vital for humans. Mineralogical studies show that pharmaceutical clay is composed of bentonite and organic substances. The variety of mineral composition in clay is not inferior to that of fruits and vegetables. Various types of clay are known in Armenia. Proportions of mineral substances in clay are universal, and combinations are unprecedented [2]. Natural clay has a more heterogeneous composition. Natural clay is rich in U, V, Cd, Mo, Tl, Ag, Ni, Cu, Sb, As, S, Se, and Br. Therefore, the oral use of clay can not be dangerous [3]. Armenia is rich in deposits of various types of clay. There are known deposits of Noyemberyan bentonite clays and zeolites, deposits of bentonite clays in Sarigyugh, etc. [4].

An excellent illustration of the origins of geophagy can be found in the legends related to the therapeutic properties of the clay from Chimayo, New Mexico. X-ray diffraction analysis of 22 samples from New Mexico, North America, and worldwide showed highly variable clay mineral compositions. One could be a complicated mixture of illite, kaolinite, smectite, chlorite, and vermiculite, while the other could be a monometallic smectite or kaolinite. The quantities of elements (Al, Si, K, Na, Ca, Mg, Fe, Mn, Ti, P, S, Ba, Sr, Pb, Zn, Cd, Co, Cu, Cr, Ni, V, Zr, Se, Mo, Be, Sb, and As) extracted by 0.12 M hydrochloric acid varied from approximately 1.0 mg/g to the limit of detectability, 0.0001 mg/g. Potential long-term human health effects were evaluated with the Reference Dose Ratio (RDR). It divides the quantity of the element extracted from 50 g of the total sample by the recommended reference dose (RfD) reported in the Environmental Protection Agency's (EPA,

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USA) IRIS (Integrated Risk Information System) database. For Na, Cr, Sb, and As, the median RDR values were higher than 1.0, suggesting an abnormally high potential intake. Given the variety of substances humans ingest, care should be taken when comparing the findings of one clay study to those of another without considering the mineralogical and chemical information [3].

With the worldwide rise of infectious diseases and the growing number of antibiotic-resistant bacterial strains, the need for precise identification, prevention, and efficient treatment is more vital than ever.

In recent decades, the misuse of common antibiotics has driven the need to discover new inhibitory agents. Therefore, natural products such as clays exhibiting antibacterial properties are prominent. By annihilating bacteria and absorbing harmful substances and gases, clay cleanses the body of toxins, slags, and heavy metals. It has a strong antibacterial and antitumor effect. It refers to benign (tumors like tresses, fibroids, mastopathy, etc.) and malignant (cancerous) tumors. Supposedly, it is because the clay contains radium. Human body needs it in small, limited doses. It is possible that clay, as a natural sterilizer, acquired its bactericidal effect with the presence of radium [4].

The absorbing properties of clay minerals are well manifested for skin and gastrointestinal disease treatment. However, the antibacterial properties of clay have attracted less attention from scientists.

Recently, French green clay has been proven to cure Buruli ulcer, a necrotic or "meat-eating" infection caused by *Mycobacterium ulcerans*. Evaluation of the antibacterial properties of this clay can provide effective and affordable treatment of Buruli ulcers and other skin infections [5].

Experiments involving the extraction of carbonate-hosted clay materials resulted in a wide range of laboratory protocols (e.g., hydrochloric acid, acetic acid, formic acid or cation-exchange resins). Refraction is emphasized as the main factor when studying the significance of clay minerals for palaeoenvironmental and diagenetic interpretations. Experiments show that in the case of mixed carbonate-clastic facies, the relative increase in intensity peaks of quartz pseudomorphs (where present) hides the further identification of non-carbonate minerals. Today, the dimension is observed despite the effective dissolution of calcite in cases of higher concentrations of acetic acid.

For calcite-dominated lithologies (oolitic limestone), the use of acetic acid at higher concentrations resulted in the most efficient decarbonation [6].

To determine the most promising natural types of clay in Armenia, some experts have provided comparative analyses of their composition and usage suggestions [2].

▪ Clay from the Artik region: Color - white with a pinkish tint, odorless, consistency - dense. Composition - sulfate-hydrocarbonate-sodium, pH - slightly alkaline. Mineralization - 1.3 g/dm³; (SO₄ - 70 mg/eq%; HCO₃-23 mg/eq%; (Na + K) - 83 mg/eq%); pH 8.43. Emission spectral analysis showed the presence of the following chemical elements (in%): Si- 3.5-4.5, Ca- 0.1-0.25, Ni- 0.001, Al- 1.5-3.5, Fe- 2,5-3.5, Cr- 0.05-0.75, Mg- 0.32-3.0, Mn - 0.18-1.8, Mo- traces, Ti- 0.016-0.56, Sr -0.0075-0.0085. Microbiological parameters are in normal state. The presented composition enables one to attribute clay from the Artik region of the

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Republic of Armenia to the category of natural remedies and recommend its use in restorative therapy.

▪ Clays from Voghjaberd area of Kotayk Marz:

Sample I. Colour - white, consistency - dense, composition - sulfate-calcium-sodium, contains metasilicic and orthoboric acids, pH - slightly alkaline. Mineralization -4.8 g/dm³, SO₄ - 2116.756 mg/dm³, Ca -521.04 mg/dm³, (Na+K) - 507.15 mg/dm³, H₂SiO₃ - 47.0 mg/dm³, HBO₃ -11.0 mg/dm³, pH 7.8.

Sample II. Colour - white, consistency - dense, composition - sulfate-calcium-sodium, contains metasilicic and orthoboric acids, pH - slightly alkaline. Mineralization -2.5 g/dm³, SO₄ - 4131.46, Ca 569.136, (Na+K) - 2538.28 mg/dm³, H₂SiO₃ - 43.0 mg/dm³, HBO₃-11.0 mg/dm³, pH 8.19.

Microbiological parameters are in a normal state. The studied samples, in particular, Sample I, can be recommended for the treatment of articular pathologies and metabolic disorders in the form of clay-water baths and applications. The alkaline reaction and the bioactive components in all samples provide a basis for a deep and more comprehensive study of local origin clays before they could be recommended for use in clinical experience.

The effect of salt on the surface properties of clay minerals depends on the nature of the mineral, the properties of the salt used, and its state (in solution or adsorbed). It has been proven that the treatment of clay minerals with NaCl, MgCl₂, Ca(CH₃COO)₂, and ZnCl₂ solutions lead to an increase in their water-holding capacity: NaCl > MgCl₂ > Ca(CH₃COO)₂ ≈ ZnCl₂ [7].

It should be noted that in the Armenia there are still no technical regulations developed for the natural resources of the crust, particularly the requirements for natural healing clays, the order of use, conditions, and requirements of the raw materials classified and extracted. The exploitation of these resources violates all the technical regulations adopted for the operation of such mines. For this reason, it is necessary to register the results of studies of therapeutic mud in resort (sanatorium-resort) zones [8].

Rock salt reserves in Armenia amount to several billion tons. The Avan salt mine is big. It is located in the northeastern part of Yerevan. It has been known since 1949; industrial exploitation began in 1967. The Miocene sedimentary layer included in the geological structure of the Avan salt mine is expressed by the alternation of clay and rock layers and forms steep flanks and meridian-spreading brachyanticlinal folds.

The thickness of the alluvial stratum is 700 m, and the thickness of the exploited salt strata is 2-50 m.

In the geological structure, dolomite and andesite basalts of the Pliocene, with a capacity of about 220 m and partly Pleistocene, are present [9]. In the **Republican Speleological Therapeutic center** operating on the base of the Avan salt mine, bronchial, pharyngitis, bronchitis, and other diseases are treated [10]. The rock salt for the cattle breeding (no less than 93% of sodium chloride) and ground salt (no less than 90% of sodium chloride) for technical purposes in the plant's mine at a depth of 300 m.

Technical rock salt

Mass portion of sodium chloride, %, no less than	93,0
Mass portion of calcium-ion, %, no more than	0,8
Mass portion of magnesium-ion, %, no more than	0,8
Mass portion of sulphate-ion, %, no more than	2,0
Mass portion of substance which is insoluble in water, %, no more than	5,0
Mass portion of humidity, %, no more than	0,4

In the first stage of table salt production, the physical and mechanical mixture solution formed by dissolving the rock salt in water is subjected to purification to remove the residue of carbonate-sulfate-clay mineral origin, which is insoluble in water (Fig. 1).

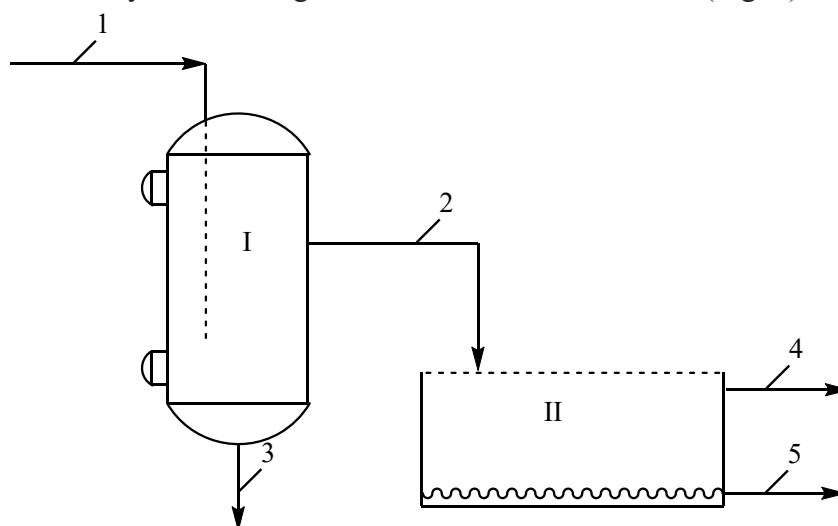


Fig. 1 Principal diagram of the purification technology cycle from carbonate-sulfate-clay mineral residues

Material flows: 1. Initial physico-mechanical mixture-solution, 2. The mixture-solution cleaned from coarse mixtures and sand, 3. Sand residue, 4. Solution purified from mechanical mixtures for further processing, 5. Fine-grained clay sediment I - Apparatus for catching and separating coarse mixtures and sand, II - Fine-grained clay mixture settling tank (open basin)

Conflict Setting

The study aimed to identify the possibilities of using the bottom sediment separated during the extraction of table salt from the rock in the Avan salt plant as basis for the composition of healing clays, skin care cosmetic products, skin scrubs, and anti-inflammatory and pain-relieving balms, analgesic, anti-aging products. The task of the study is to expand the list of physiotherapeutic clay therapy products containing a new mineralized clay component and several supplements of natural origin.

Research Results

The study of bottom deposit clay separated during the production of table salt from rock salt was carried out in the Laboratory of Natural Technologies at Shushi University of

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Technology. The Avan salt plant fine-grained clays were sampled to determine their physical and chemical characteristics, as for the content analysis of microelements, it was done at the Yerevan Hydrometeorology and Monitoring Center (Tab. 1).

The quantity of microelements in the sample was determined by inductively coupled plasma mass spectrometry (ICP-MS), using the PerkinElmer ELAN 9000 device, in the following operating mode: vacuum - $1.5-2.5 \cdot 10^{-7}$ torr, argon plasma power - 1400 W, dust sprayer gas flow - 0.76-0.8 l/min, plasma-generating gas flow - 20 l/min, ambient temperature - 15-30 °C, cooling liquid flow - 13.5 l/min, cooling liquid pressure - 350 kPa, coolant temperature - 15 °C, argon purity - >99.996%. The results of the examination are presented in Tab. 2.

Table 1

Physical and chemical characteristics of bottom deposit

№	Measured indicator	Measuring unit	Measured value	Applied method by standard
1	Dry residue (180 °C)	%	61.44	ISO11923
2	Dry residue (420 °C)	%	60.31	ISO11923
3	Electroconductivity - in aqueous distillate	µS/cm	483000	ISO7888 ISO11265
4	Mineralization - in the aqueous distillate	mg/kg	314000	
5	pH - in the aqueous distillate	-	7,46	ISO10523 ISO10390

According to the findings of laboratory studies of sedimentary clay, we used it in the composition of anti-inflammatory, pain-relieving balms and creams (scrubs) for skin scrubbing.

In order to improve the healing properties of clay, natural antibacterial and pain-relieving additives were used in healing balms with a clay base: 20% alcohol solution of propolis and essential oil of laurel, and the ingredient "Dimexide" (dimethylsulfoxide) was used to make skin tissues more permeable. Thus, the invention of Kavalgin balm was developed and registered, which refers to an anti-inflammatory, pain-relieving agent analgesic means, in particular, it is a new preparation for treating various joint disorders, neuritis, neuralgia, osteochondrosis, sciatica and other inflammations and pains.

Skin care products are mentioned in the development of the scraper ointment with clay component content. This natural ointment is a skin-cleansing, regenerating anti-inflammatory agent that is especially designed for scraping and cleaning dead skin cells, curves, and is a way to reduce the appearance of age wrinkles nourishing the skin and increasing elasticity. The cream is a combination of only natural ingredients. It exhibits pronounced protective and regenerating properties, it also has antioxidant, free radical neutralizing properties. The cream includes clay sediment containing more than 30 microelements from the processing of the Avan salt mine, lanolin, vaseline, glycerin, 20% sweet marjoram extract, grape and milk thistle seed oils.

Table 2**Composition of microelements in the bottom deposit**

№	Measured indicator	Unit	Measured value
1	Lithium	mg/kg	6,03
2	Beryllium	mg/kg	0,0502
3	Boron	g/kg	0,204
4	Sodium	g/kg	1,72
5	Magnesium	g/kg	0,262
6	Aluminum	g/kg	0,0150
7	Total Phosphorus	g/kg	0,240
8	Potassium	g/kg	7,27
9	Calcium	g/kg	3,38
10	Titanium	g/kg	1,37
11	Vanadium	g/kg	0,0347
12	Chromium	mg/kg	8,99
13	Iron	g/kg	0,446
14	Manganese	g/kg	0,251
15	Cobalt	g/kg	0,0137
16	Nickel	g/kg	0,11
17	Copper	g/kg	0,0337
18	Zinc	g/kg	0,0336
19	Arsenic	mg/kg	4,08
20	Selene	mg/kg	2,25
21	Strontium	mg/kg	1,42
22	Molybdenum	mg/kg	7,73
23	Cadmium	mg/kg	0,184
24	Tin	g/kg	4,47
25	Stibium	g/kg	0,863
26	Barium	g/kg	0,0976
27	Lead	g/kg	0,0155

Based on the results of bottom deposit clay laboratory studies, we used it in the composition of anti-inflammatory and pain-relieving balms and skin scraping cream (scrub). To improve the healing properties of clay, a natural antibacterial and pain-relieving additives were used in healing balms with clay bases: a 20% alcohol solution of propolis and laurel essential oil was used, and the "Dimexide" (dimethylsulfoxide) ingredient was used to activate the permeability of skin tissues. Thus, the invention of "Kavalgin" balm was developed and registered, which refers to an anti-inflammatory pain reliever and is a new preparation for treating arthropathy, neuritis, neuralgia, osteochondrosis, radiculitis, and other inflammations and pains [11]. The invention of another preparation developed with clay, such as scrub ointment, refers to skin care products. This natural ointment is a skin-cleansing, regenerating, and anti-inflammatory agent, specifically for removing dead skin cells, smoothing wrinkles, nourishing the skin, and increasing elasticity. The ointment contains only natural ingredients and exhibits protective and regenerating properties. It also has antioxidant and free radical-neutralizing properties. The ointment includes clay sediment containing more

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than 30 microelements from the processing of the Avan salt mine, lanolin, vaseline, glycerin, a 20% alcoholic extract of Origanum, grapeseed and milk thistle seed oils [12].

Conclusion

The qualitative-quantitative characteristics of the bottom sedimentary clay of the Avan salt mine, the effectiveness of the new healing balms developed with clay support allow us to conclude that the separated clay bottom sediment has healing and cosmetological properties. It is ecologically, toxicologically safe and can be used to create skin care products and medicines. On the basis of the separated mineralized clay sediment, we also find it promising for the creation of preventive toothpastes, gums, care for the teeth and oral cavity, in particular, sanitation of the oral cavity, elimination of unpleasant odor from the mouth, teeth whitening anti-inflammatory agents.

Based on the separated mineralized clay sediment, we also find it promising for the creation of prophylactic toothpastes, gums, teeth and oral cavity care, particularly oral cavity renewal, bad breath elimination, teeth whitening anti-inflammatory products.

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**ԱՎԱՆԻ ԱՂԻ ՀԱՆՔԻ ՀԱՏԱԿԱՅԻՆ ՆՍՏՎԱԾՔԻ ԿԱՎԻ ՀՆԱՐԱՎՈՐ
ԿԻՐԱՌՈՒԹՅՈՒՆԸ ԲՈՒԺԻՉ ԿԱՎԵՐԻ ՈՒ ԿՈՍՄԵՏՈԼՈԳԻԱՅԻ ՄԵՋ**

Ներսիսյան Գ.Հ.¹, Ֆարսիյան Ն.Վ.¹, Հակոբյան Գ.Գ.², Նավթալյան Ի.Գ.¹, Միքաելյան Ա.Ռ.³

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Կավի բուժիչ և կոսմետիկ հատկությունները հայտնի են դեռևս հին ժամանակներից: Կավի բուժիչ և կոսմետիկ հատկությունները օգտագործվում են տարբեր հիվանդությունների բուժման և մաշկի որակը բարելավելու համար բուժիչ նպատակներով: Սույն աշխատանքի նպատակն է ուսումնասիրել բարձր հանքայնացված կավի քանակական բաղադրությունը, որը Երևանի Ավան աղի հանքում արդյունահանվող հումքի վերամշակման ընթացքում առանձնացված հատակային նստվածք է, և բացահայտել դրա կիրառման հնարավորություններն ու շրջանակը: Փորձարարական տվյալների հիման վրա մշակվել են թերապևտիկ կավի, հակաբորբոքային միջոցների, ցավազրկող բալասանների, կոսմետիկայի և մաշկի սկրաբների բարելավված հատկություններով պատրաստուկային ձևեր՝ օգտագործելով բարձր հանքայնացված կավի և բնական հավելումների կայուն համակցություններ:

Բանալի բաներ. քարաղ, միներալացված կավ, ակնամոմ, միկրոտարրեր, հակաբորբոքային միջոց:

**ПЕРСПЕКТИВЫ ПРИМЕНЕНИЯ ВЫСОКОМИНЕРАЛИЗОВАННОЙ ГЛИНЫ
ДОННЫХ ОТЛОЖЕНИЙ АВАНСКОЙ СОЛЯНОЙ ШАХТЫ В
ЛЕКАРСТВЕННЫХ ГЛИНЯХ И КОСМЕТОЛОГИИ**

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Лечебные и косметологические свойства глин известны с древних времен. Лечебные и косметические свойства глины используются для лечения различных заболеваний и в лечебных целях для улучшения качества кожи. Целью данной работы является изучение количественного состава высокоминерализованной глины, представляющей собой донный осадок, отделяемый при переработке сырья, добываемого на Ереванской Аванской соляной шахте, и выявление возможностей и сферы ее применения. На основе экспериментальных данных разработаны рецептуры лечебных глин, противовоспалительных средств, обезболивающих бальзамов, косметических средств и скрабов для кожи с улучшенными свойствами с использованием стабильных комбинаций высокоминерализованной глины и натуральных добавок.

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Ключевые слова: каменная соль, минерализованная глина, микроэлементы, прополис, противовоспалительное средство.

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