

Survey of Soviet Activity in the Use of Active Chemicals for Space Cabin Air Revitalization

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The Soviet manned space flights have relied on an "active chemical" for the maintenance of a habitable cabin atmosphere. The "active chemical" has not been specifically identified in the available Soviet published literature. However, reasonably detailed descriptions of the properties of the "active chemical" have been given and, on the basis of those descriptions, it is concluded that the material employed was an alkali metal superoxide.

Soviet scientists have been active for many years in the study of inorganic peroxides, superoxides, and ozonides as air revitalization materials. This activity is reviewed and the significance of current Soviet basic chemical studies to future chemical air revitalization systems is analyzed.

THE AVAILABLE SOVIET popular and technical literature related to the Soviet man in space programs has consistently referred to the use of "active chemicals" as the prime method of maintaining habitable atmospheres in Soviet space cabins. In this paper the Soviet activity in the area of chemical means of air revitalization is reviewed. The term "chemical means of air revitalization" is herein defined as the use of multifunctional chemical compounds suitable for use as sources of oxygen and for carbon dioxide removal in manned space cabins. Of particular interest in this regard are inorganic peroxide, superoxide, and ozonide compounds.

In reading this survey, it must be remembered that the life support potential of inorganic peroxide, superoxide and ozonide compounds is not the only important characteristic of these compounds. They are, in general, strong oxidizing agents and strong bases, and could be useful in a wide number of applications, such as high energy oxidizers for propulsion purposes, and in the chemical process industry. Therefore, the motivation for studying these compounds is not necessarily restricted to life support.

The Russian literature in the area of chemical means of air revitalization indicates clearly their willingness to invest in long term basic research projects in an effort to develop chemicals to supply oxygen and/or absorb carbon dioxide and water vapor. One is struck by the quality and quantity of published Russian literature dealing with basic research investigations concerned with the chemistry of the synthesis of inorganic superoxide, ozonide, and peroxide compounds, and

with the thermodynamics and kinetic studies of the pertinent air revitalization chemistry of these materials. Numerous publications have appeared dealing with the nature and the rates of the reactions of these materials with carbon dioxide, carbon monoxide, and water vapor.¹⁻⁶³

It would be safe to estimate that since the early 1950's the Russians have outpublished U. S. scientists by about 3:1 in regards to basic research on these materials. At least one of their leading scientists in this area, I. A. Kazarnovskii,⁴⁻¹⁵ who has been active in this field since the early 1930's, has received public acclaim for his work. In an article entitled "Toward New Achievements in Soviet Chemistry," which appeared in Pravda, June 25, 1962, Kazarnovskii is praised as a major inorganic chemist. His work on superoxides was especially noted and he was credited as being responsible for the current industrial scale production of sodium superoxide in Russia.

Analysis of the Russian literature, both the technical literature and that prepared for general public consumption, leads this author to conclude that the great attention they have given to active chemical compounds for air regeneration has been rewarded handsomely. The most dramatic reward has been the use of superoxides by the Russians in the life support systems of the Vostok and Voskhod vehicles. Instead of using a reduced-pressure, all-oxygen atmosphere, as in the case of our Mercury and Gemini vehicles, the Vostoks employed slightly oxygen-rich air at normal pressure, and regenerated the oxygen by means of an "active chemical."⁴⁴ It must be pointed out that, as far as can be discovered, nowhere in the Russian literature describing Russian manned space flights is the source of breathing oxygen employed specifically identified as a superoxide. However, careful analysis of their available published works very clearly points to the use of unfamiliar oxidation state compounds of the alkali or alkaline metal superoxide or peroxide, or of the alkali metal ozonide type. Specifically, it appears that the compound of choice was sodium superoxide. Volynkin, et al.,⁶¹ point out that "at the present time, highly efficient regeneration substances are able not only to give off oxygen to exchange for that used in breathing, but also to absorb, simultaneously, great quantities of CO₂ and moisture. In addition, these substances, as research has shown, have the ability to oxidize and absorb certain harmful gaseous products formed in the course of human vital activity."

From General Dynamics/Electric Boat Div., Groton, Connecticut.

Volynkin lists among the important advantages ascribed to the air revitalization systems of the Vostoks the following:

1. Efficiency of operation at a temperature of $20 \pm 10^\circ\text{C}$., a relative humidity of 30 to 70 per cent, and a barometric pressure of 760 ± 50 mm. of Hg.
2. Absorption of gaseous products liberated in the course of human vital activity.
3. Resistance to the influence of vibration and high overloads; heat and explosion resistance.
4. Simplicity of construction.
5. Minimum power consumption.
6. High operational reliability.
7. Complete automation of process for maintaining the required microclimatic conditions.

In addition to the "active chemical" described above, the Vostoks required an additional chemical for humidity control of the cabin. This fact serves as more evidence that the "active chemical" is an unfamiliar oxidation state compound since inorganic superoxide, peroxide, or ozonide compounds would not be sufficient to maintain the conditions of relative humidity specified above. In the words of Volynkin, et al., the problems associated with the use of *active compounds* were "in principle and in practice, solved in preparing and conducting the biological experiments in the two earth satellites." Seryapin writes that "the application of *chemical substances* (italics ours), capable of simultaneous absorption of moisture and carbon dioxide and liberation of oxygen is quite economical in comparison with other systems." He goes on to offer that systems based on liquid oxygen and gaseous oxygen would be

"3.5 and 8 times as heavy," respectively, as a system based on the use of these so-called "active chemical compounds."

A schematic diagram of the air revitalization system employed in the manned Soviet space flights is shown in Figure 1. The system evolved as a result of laboratory experiments with animals, dogs weighing 5-7 kg. In the early phase of development the number of tests conducted appear to be numerous. Seryapin relates that in the majority of these early experiments, numerous difficulties with the use of the "active chemical" developed and were systematically overcome.

The difficulties spelled out in the Seryapin report are the type of problems known to be associated with superoxide systems. The two main problems were overproduction of oxygen and non-uniform utilization of the "active chemical." They found that they could overcome these difficulties by breaking up the required charge of "active chemical" into sections each providing 2-3 days oxygen supply. Thus, as the substance in one section became exhausted, it could "automatically" be switched off and the cabin air allowed to flow through another section. The problems associated with the "automatic control" of such a technique, as well as weight and volume considerations, eliminated the implementation of this solution.

The method of utilization finally settled upon was to split the "active chemical" charge into two units and to use a controlling aneroid to switch one of the units on or off. Thus the atmospheric pressure in the cabin was used as the controlling variable in the operation of the air revitalization unit. Increase of the pressure above 765 mm Hg (the predetermined level) was taken to indicate an increased rate of oxygen production and one of the "active chemical" beds was turned off by preventing the cabin air from flowing through it. Conversely, both units were allowed to operate when the pressure fell below 765 mm Hg. Seryapin reports that this method of ventilation "works faultlessly and is stable." The use of the cabin pressure for the control of the rate of oxygen production is obviously predicated on the maintenance of a constant cabin air temperature and a very small cabin leak rate.

In 1963 a publication in *Khimicheskaya promy shlennost'* (No. 5, pp. 73-74) described the development of a glass wool filter for trapping potassium superoxide dust. The filter was designated as an FS-8.5 filter and is claimed to be very effective. The significance attached to the development of this filter would appear to be that the Russians are making wide use of KO_2 in cannister type systems. The dusting problems associated with the use of this material seem to have been solved by the use of the FS-8.5 filter. This particular article is of further interest in that it is one of the few appearing in the open literature that deals with a specific engineering problem. As mentioned above, most of their publications are very basic in nature.

A clear insight of Russian activity in the study of inorganic superoxide, peroxide, and ozonide compounds can be gained from a study of the published proceedings of the second conference on the "Chemistry of

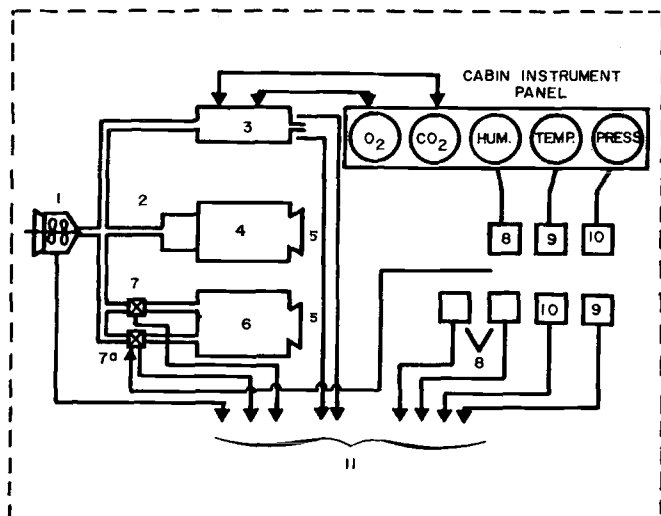


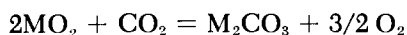
Figure 1. Schematic Diagram of the Air Regeneration System used in Vostok Cabins (From Volynkin, Yu. M., et al, "The First Manned Space Flights," Moscow, (1962)). 1. Fans, 2. Regulator, 3. Automatic CO_2 and O_2 Analyzer, 4. "Active Chemical" Regenerator Unit, 5. Dust and Harmful Impurities Filters, 6. Dehumidifier Unit, 7. Damper, Manually Controlled, 7a. Damper, Automatically Controlled (Set to open at 70% R.H. and to close at $35 \pm 5\%$ R.H.), 8. Humidity Sensors, 9. Temperature Sensor, 10. Pressure Sensor, 11. Remote Control Signals to and from Earth. Note: Aneroid control of regenerator not depicted.

Peroxide Compounds," held in Moscow on November 14-18, 1961 and published in 1963. In the introduction to these published proceedings, the conference was described as "the first important meeting (on peroxide compounds) not only in the USSR, but also abroad." The conference was sponsored by the Institute of General and Inorganic Chemistry of USSR Academy of Sciences, by the Scientific Research Institute of Chemistry at the Gorky State University, and by the Scientific Research Institute of Basic Chemistry of the State Committee on Chemistry attached to the Council of Ministers of the USSR. More than 300 representatives from 60 scientific research institutes, higher scientific establishments, and industrial enterprises from 29 cities of the Soviet Union participated. In the closing paragraph of the introduction to the published proceedings, the following call was made for concentration of the research effort: "Research of inorganic chemists should be directed toward synthesis of new superoxides and ozonides rich in active oxygen, synthesis of other peroxide compounds which would enable uncovering regularities of their formation. In this research, it would be necessary to apply superhigh pressures of oxygen, ozonized oxygen, concentrated hydrogen peroxide in anhydrous solutions, and electrochemical methods."

A number of papers delivered at that conference along with other published reports serve to confirm the continuing Russian interest in the following areas:

1. *Synthesis of alkaline earth superoxides, notably calcium superoxide.* Results to date indicate that the Russians have not succeeded in synthesizing this compound in greater than 40-50 per cent purity. In this regard, American investigators may have been somewhat more successful. Both R. R. Miller of the Naval Research Laboratories and Dr. A. W. Petrocelli, GD/EB, have claimed 50-60 per cent purity. High purity calcium superoxide (85-100 per cent) would be superior to both potassium and sodium superoxides as an air revitalization material.

2. *Study of carbon dioxide-superoxide reaction.* The effort in this area appears to be directed to developing a good basic knowledge of this important air regeneration reaction. The stoichiometric reaction generally written is:

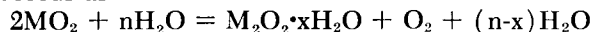


It is known, however, that the reaction is far more complex than indicated by the stoichiometry written above. In addition to alkali metal carbonates, it is known that bicarbonates, MHCO_3 , also form. If the reaction conditions favorable for the controlled formation of bicarbonate could be established, then the capacity for CO_2 absorption of a superoxide system could be greatly enhanced. This line of reasoning in part, may explain at least, the motivation of Russian workers involved in detailed basic studies of $\text{KOH} - \text{CO}_2 - \text{H}_2\text{O}(\text{v})$ and $\text{MO}_2 - \text{CO}_2 - \text{H}_2\text{O}(\text{v})$ reaction systems.

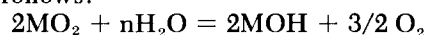
In this same regard the Russians have shown interest in the study of the formation and nature of alkali metal compounds of the peroxocarbonate type; principally sodium and potassium peroxodicarbonates ($\text{M}_2\text{C}_2\text{O}_6$) and the peroxomonocarbonates, MHCO_4

and M_2CO_4 . They have claimed to have prepared potassium and sodium peroxodicarbonate ($\text{M}_2\text{C}_2\text{O}_6$) via the reaction of potassium or sodium superoxide with water and carbon dioxide at 0°C . They attach two points of significance to this result:

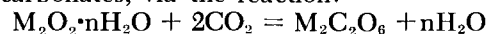
(a) Verification of the fact that at low temperatures, -20°C to 0°C , the reaction of superoxides with water proceeds as follows:



This reaction is significant since it establishes the fact that in the temperature range indicated, superoxides, upon reaction with water vapor, will form stable peroxide compounds ($\text{M}_2\text{O}_2 \cdot x\text{H}_2\text{O}$), thereby diminishing their oxygen yield. This is in marked contrast to the results obtained when superoxides are caused to react with water vapor at higher temperatures, i.e., room temperature and above. In this case, the reaction proceeds as follows:

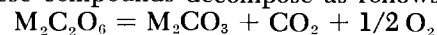


The Russians reasoned that the presence of the peroxide compounds in the reaction mixture, at the low temperature, should be conducive to the formation of peroxocarbonates, via the reaction:

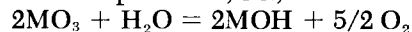


Thus, by demonstrating the formation of $\text{M}_2\text{C}_2\text{O}_6$ via the reaction of $\text{MO}_2 + \text{H}_2\text{O} + \text{CO}_2$ at 0°C they have established the correctness of the mechanism for the reaction of MO_2 and water at low temperatures.

(b) Their second point is concerned with the discovery of a new and simple method for the production of alkali metal peroxocarbonates. These compounds may be of industrial value. It may also be mentioned that in addition to the points made above, this work may also be motivated by the intriguing possibility that if the reaction of CO_2 with alkali metal hydroxides and carbonates or oxides could be controlled to yield significant amounts of the peroxodicarbonates, then it may be possible to establish a regenerative CO_2 scrubbing system based on these materials. Differential thermal analysis studies of sodium and potassium peroxodicarbonates have been reported in the Russian literature. These studies establish that at relatively low temperatures, these compounds decompose as follows:



3. *Search for and study of new compounds rich in active oxygen.* Russian scientists continue to show considerable interest in alkali metal ozonides, MO_3 . These compounds have been shown to react in a manner analogous to the superoxides, i.e.,



The Russians must be considered the leaders in the area of inorganic ozonide chemistry, and it appears, from the available published literature, that many of the Russian scientists who made major contributions to the superoxide field have also been active in the ozonide field, i.e., Kazarnovskii, Makarov, etc.

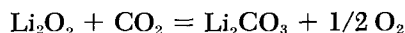
In an article appearing in *Priroda* (Nature) in December 1963, entitled "Ozone in the Service of Large-Scale Chemistry," by Iu. N. Emel'ianov, the claim is made that alkali metal ozonides are already finding application in the Soviet Union as "oxidizing agents, bleaching material, as catalysts in certain polymeriza-

tion reactions, and *also as sources of oxygen in insulated places where the regeneration of air is required: in the cabins of spacecraft, in autonomous diving suits, etc.*" (italics ours).

However, we question the implication derived from the above claims which would indicate that such ozonides are being prepared in very large quantities. Examination of publications in this field gives no indication whatever that the Russians have succeeded in adapting, to large scale production, the known method of ozonide formation, i.e., the reaction of ozone gas with solid alkali metal hydroxides followed by extraction of the prepared ozonide from the greater mass of unreacted solid hydroxide with liquid ammonia. In the same article, it is mentioned that "As yet, no methods are known for getting these substances (inorganic ozonides) without the use of ozone." This note indicates that they do not have, but are trying to develop better methods for ozonide production. They have not as yet, as far as we can discover, reported such attempts in the open technical literature. The major significance to be placed on the Soviet claims, however, is that, beyond any question, the Russians do recognize the potential of these materials for life support and other industrial use and are actively pursuing studies on the ozonide compounds. Kazarnovskii was again given public recognition for his work in this field in the *Priroda* article.

The overall conclusion drawn from the Soviet publications in this field is that it is very doubtful that they have as yet succeeded in advancing the state-of-the-art to the point that alkali metal ozonide compounds are actually being used for life support purposes.

Russian literature also reflects an interest in the synthesis and chemistry of peroxide compounds, M_2O_2 . Extensive studies of lithium peroxide, Li_2O_2 , chemistry have been carried on at the Institute of General and Inorganic Chemistry of USSR Academy of Science. In 1964, T. A. Dobrynina published a monograph devoted to Li_2O_2 chemistry. Li_2O_2 has a particularly attractive life support potential which has certainly not escaped the attention of the Russian investigators. The compound is known to react with carbon dioxide, i.e.,



Its potential as a CO_2 scrubber and oxygen source is apparent. The state-of-the-art with respect to the use of this compound for life support purposes is not very advanced and little that has appeared in the Soviet open literature would lead us to believe that they are very much ahead in the field of peroxide chemistry. Lithium peroxide was studied in the U. S. in 1963 under a Wright Air Development Center contract by the Foote Mineral Company.

SUMMARY

The Soviets have been rewarded for their years of basic and fundamental research on superoxides by successfully developing these materials for use in life support systems of spacecraft.

Their literature demonstrates that they are continuing their efforts to improve on what they have by (a) search for new compounds suitable for life support systems, i.e., new superoxides, peroxides, and ozonides, (b) improving the operation of superoxides systems and (c) search for new and better CO_2 absorbers.

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