

Carbon Dioxide in New Mexico

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PHYSICAL PROPERTIES

The physical properties of carbon dioxide are discussed in various publications. Some of the more important physical properties and those of particular interest in connection with the manufacture and use of solid carbon dioxide, or "Dry-Ice" are given below:

Carbon dioxide at ordinary temperatures is a colorless, invisible, non-combustible and odorless gas. It is different from water in that it cannot exist as a liquid at atmospheric pressure. On the other hand, it can exist as a solid at atmospheric pressure provided its temperature is sufficiently low.

Carbon dioxide is white in color and resembles snow. Instead of melting to a liquid, as ice does, it sublimates, passing directly from the solid to the gaseous state. Because no liquid is involved in the process "Dry-ice" does not wet containers, packages or materials refrigerated, which property is one of its great advantages.

The specific gravity of carbon dioxide gas is 1.52. The specific gravity of the liquid varies considerably depending on the temperature, the higher temperatures being characterized by lower specific gravities. At 30° C. the specific gravity is 0.598. At -10° C. the specific gravity is 0.981 and at -60° C. it is 1.191. The specific gravity of crystalline carbon dioxide made by freezing liquid carbon dioxide is 1.53, but the specific gravity of the commercial product, consisting of cakes formed by compressing the loose "snow" is about 1.25. Ordinary ice has a specific gravity of 0.9.

The temperature of "Dry-ice" at a pressure of one atmosphere is -109° F. (-78.5° C.). "The triple point," or the point at which carbon dioxide is in a sense simultaneously a solid, liquid and gas, is when it has a temperature of -69.88° F. and a pressure of 75.13 lbs. per sq. in.

Above 88° F. it is impossible to liquefy carbon dioxide gas by pressure alone. The gas liquefies at a pressure of 1,100 lbs. per sq. in. at 70° F., but under certain conditions, including lower temperatures, it may be liquefied at somewhat lower pressures.

The relative refrigerative effects of "Dry-ice" and ordinary water ice have been stated by a number of investigators, and some of these statements are quite contradictory. Circular LC-286 of the U. S. Bureau of Standards states that "one pound of solid carbon dioxide has approximately the same refrigerating effect at 32° F. as two pounds of ice." This same statement is made by J. C. Miller in Technical Publication No. 736 of the American Institute of Mining and Metallurgical Engineers. It is based on the following data:

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(1) The heat of fusion of water ice, or the heat absorbed in its change from the solid to the liquid state with no change in temperature, at 32° F. is 144 B.t.u. per lb.

(2) The heat of vaporization of "Dry-ice," or the heat absorbed in changing it from a solid to a gas, at -109° F. is 248 B.t.u. per lb. The heat absorbed in raising the temperature of the carbon dioxide gas from -109° F. to +32° F. is 27 B.t.u. per lb. Hence the total heat absorption is 275 B.t.u. '

(3) The refrigerating effect of "Dry-ice," as compared to that of ordinary ice, is therefore in the ratio of 275 to 144 or 1.91 to 1; approximately 2 to 1.

In Deming's "General Chemistry," 4th ed., p. 463, it is stated that "Carbon dioxide passes directly from the solid to the gaseous condition, and surrounds the material to be refrigerated with an insulating atmosphere of dry gas. For this reason its refrigerating effect is about ten times that of an equal weight of a mixture of ice and salt, in spite of the fact that the calories absorbed per pound of carbon dioxide vaporized are only about two times the calories absorbed per pound of ice melted."

The "Petroleum Engineer" for May, 1931, contains an article by Mr. K. C. Sclater, entitled "Natural Gas Supply for Manufacture of Dry Ice." In this article Mr. Sclater, who is editor of the "Petroleum Engineer," states that "as a refrigerant, one pound of solid carbon dioxide is almost as efficient as 14 pounds of solid (water) ice." Mr. Sclater gave additional information in connection with this statement in a letter to E H. Wells under date of December 4 1937, as follows: "The basis for this statement is the experience gained in transporting by railroad edible goods that must be shipped in refrigerated cars. Between New York and Philadelphia it was found that 200 lb. of solid carbon dioxide did the refrigerating work of 3000 lbs. of water ice plus 600 lbs. of salt. This is an actual efficiency ratio of 15 to 1."

Several recent articles state that one pound of "Dry-ice" is as efficient as a refrigerating agent as 13 to 16 pounds of ordinary ice. Possibly an adequate theory to account for the much greater relative refrigerating value than the "2 to 1" value for "Dry-ice" has not yet been formulated.

USES

The possible uses of solid carbon dioxide, or "Dry-ice" are legion. As many as 2,000 have been enumerated and to list all of them would be beyond the scope of this paper.

To date the industrially important uses which absorb the bulk of carbon dioxide produced and which are economically feasible under conditions of cost and volume of market existing, are (a) the carbonation of beverages (which is largely accomplished by the use of the liquid form transported in steel cylinders); and (b) the refrigeration of ice cream (which utilizes "Dry-ice.") Smaller markets have been developed in connection with the refrigeration of meat, fish and frozen foods; charging compression refrigeration systems, mining coal, fire extinguishing, special low temperature operations, and the packing of food products in inert atmospheres.

of refrigeration.

"Dry-ice" is a potential competitor of water ice and of various mechanical refrigerating devices. "Dry-ice" may become a common household refrigerant. It may be the answer to economical air-conditioning in residences. Much progress already has been made in solving the attendant mechanical difficulties and no engineering impossibilities are likely to be encountered in handling the others.

ECONOMIC FEATURES OF "DRY-ICE"

In common with all other mineral products, "Dry-ice" must have certain valuable inherent properties, and it must be procurable at a cost in keeping with the service it renders. For a number of uses, "Dry-ice" has such outstanding advantages that its present high cost to the consumer (4 to 10 cents per lb.) is not objectionable.

As noted by E. L. Quinn and C. L. Jones in their book, "Carbon Dioxide," efficient distribution is a more important factor than efficient manufacture in the "Dry-ice" industry. Evaporation of "Dry-ice" begins at the moment of its manufacture and continues until the material is all converted into the vapor form. This characteristic brings about distribution problems not characteristic of other commercial products. Evaporation losses are greatly affected by the mass of material handled, and the smaller the unit the greater is the percentage of material vaporized.

According to Quinn and Jones, the "settled" loaded car loss, when "Dry-Ice" is transported in properly designed railroad cars of the refrigerator type, varies from 0.75 per cent to 1.25 per cent per day. Losses during truck transportation are probably somewhat greater. The evaporation losses while the "Dry-ice" is being transferred and otherwise handled are of course considerable, but they are difficult to evaluate. The same authors are of the opinion that "Dry-ice" can be stored in suitably designed storage buildings with a loss of 20 percent or less for the period from February to July.

Obviously, the New Mexico markets for "Dry-ice" are limited, and large-scale operations will depend on marketing chiefly in other states. New Mexico "Dry-ice" will have to compete with "Dry-ice" manufactured elsewhere from carbon dioxide gas obtained from various sources.

MANUFACTURE OF "DRY-ICE"

"Dry-ice" can be made by a number of processes. The one most commonly used in manufacturing it from natural carbon dioxide gas, and the one in use at the three operating New Mexico plants, is briefly as follows:

The gas, as it comes from the wells, is subjected to chemical or scrubbing treatment if necessary. It is then cooled and liquefied, following which the pressure is raised to between 950 and 1100 lbs. per sq. in. The cooled liquid is then permitted to expand in a "snow chamber" at slightly above atmospheric pressure. Less than fifty per cent of the gas entering the snow chamber forms snow, and the remainder passes out of the chamber to be recycled. The snow is compressed into cakes, after which it is ready for mar-

keting. From 20,000 to 25,000 cu. ft. of carbon dioxide gas is required to manufacture one ton of "Dry-ice."

Some New Mexico carbon dioxide is marketed in the liquid form. In the manufacture of the liquid the snow chamber is not required.

ORIGIN

Carbon dioxide gas is a very common gas and originates in many ways. It is present in the atmosphere in the amount of approximately three volumes per 10,000 volumes of air. In the hydrosphere the amount present is estimated to be about five volumes of the gas per 10,000 volumes of sea water. On this basis, the sea contains from 20 to 30 times the amount of carbon dioxide existing in the atmosphere. The carbon dioxide in the sea consists of carbonates, bicarbonates, carbonic acid and its ions, and the dissolved gas, and hence the amount of dissolved gas undoubtedly is considerably less than the above figures indicate.

Many rocks contain carbon dioxide. The rocks in which it is present in greatest amounts are the carbonate rocks, chiefly limestone and dolomite. Carbon dioxide is present in rocks having an appreciable carbonaceous content. The presence of minute inclusions of liquid carbon dioxide in igneous rocks has been reported by a number of observers.

Rocks containing organic matter may yield some carbon dioxide in connection with the processes that eventually yield coal or petroleum. Carbonate rocks, when heated by igneous intrusions or metamorphic processes, may part with their carbon dioxide content. Unquestionably vast quantities of carbonate minerals in rocks have been converted to silicates with loss of carbon dioxide.

Igneous processes are frequently accompanied by the giving off of large quantities of carbon dioxide gas. Volcanoes and springs related to igneous activity contribute much carbon dioxide gas to the atmosphere.

In the opinion of the writers, most of the carbon dioxide found in underground structures in New Mexico originated in the pre-Cambrian rocks and was due to deep-seated earth processes, igneous or metamorphic or both which took place largely in Tertiary and subsequent time. The gas may have originated tens of miles beneath the surface and under conditions that are at best highly speculative. It migrated toward the surface as an accompaniment of igneous magmas or along fissures or other openings. After entering the stratified rocks above, it was subject to the same laws as hydrocarbon gas and collected in closed structures in much the same manner. At some structures carbon dioxide gas, hydrocarbon gas and petroleum are all present

All the known promising carbon dioxide gas fields of New Mexico are in the northeastern part of the State. Carbon dioxide in notable amounts has been discovered by drilling in other states, including Colorado, Utah, California and Washington. Possibly parts of these five states can be considered to constitute "carbon dioxide provinces," in effect, areas in which deep-seated earth constituents and processes have been especially favorable for the generation of carbon dioxide and for its expulsion from the deep-seated rocks. The movement of the gas to the surface or to closed geologic struc-

tures where it has been trapped, has been in part connected directly with the upward movement of igneous magmas, but in part it may have been independent of such magmas. The parts of the "provinces," in which large quantities of carbon dioxide have risen toward the surface are probably relatively small and, as a rule, are many miles apart. This interpretation would explain the unusually large amounts of carbon dioxide present at some geologically favorable structures, as at the Bueyeros Anticline, and its absence at other equally good structures.

Keeping in mind that carbon dioxide is a liquid under pressure of more than 1,100 lbs. per sq. in. and at temperatures of less than 88° F., it is conceivable that the carbon dioxide at some of the New Mexico structures is in part present in the liquid form. If present as the liquid the carbon dioxide would weigh several times as much as an equal volume of the gas. Therefore, the carbon dioxide content of an underground reservoir would be considerably greater if it were in the liquid form than if it were present as a gas.

NEW MEXICO OCCURRENCES

Much of the information presented in this paper regarding New Mexico occurrences of carbon dioxide is summarized from Bulletin 9 of the New Mexico Bureau of Mines and Mineral Resources, "The Oil and Gas Resources of New Mexico," by D. E. Winchester, but some additional data are included, particularly in connection with the Sierra Grande Uplift, Wilcox Dome, and Bueyeros Field.

JARITAS DOME

The Jaritas Dome is located in Secs. 15, 16, 21 and 22, T. 23 N., R. 24 E., and is in the southern part of Colfax County. The closure is said to be about 40 feet.

In 1925 the California Co. drilled a test well on this structure in the southwest corner of Sec. 15, T. 23 N., R. 24 E. At a depth of 1,509 feet this well made about 500,000 cu. ft. of *gas* which contained 67 per cent carbon dioxide, 4.1 per cent oxygen, 28.7 per cent nitrogen and a small amount of helium. The well was abandoned at 2,556 feet after having penetrated several hundred feet of rock reported to be granite. The gas production in this well was probably obtained in the Upper Permian.

WAGON MOUND ANTICLINE

The Wagon Mound Anticline, in Mora County, trends nearly north-south and the crest of the structure is in Secs. 11 and 14, T. 19 N., R. 21 E. The closure is reported to be about 350 feet and approximately 35,000 acres are included within the lowest closing contour.

The Arkansas Fuel Oil Co., in 1925-26, drilled a well in Sec. 11, T. 19 N., R. 21 E. to a total depth of 2,613 feet. This well developed large amounts of carbon dioxide gas at various horizons, the estimated total amount being approximately 26,000,000 cubic feet per day. The available log of this well is evidently inaccurate, but production was probably obtained in rocks of Permian age. The well bottomed in granite or arkose.

SIERRA GRANDE UPLIFT

The Dakota Sandstone and several thousand feet of underlying strata

have been tested on a number of local structures on the Sierra Grande uplift, a large structure located in Union and Colfax Counties. No oil was obtained, but in several of the wells considerable quantities of carbon dioxide were reported. The Sierra Grande Oil Corp. drilled a well on the Sierra Grande uplift, in Sec. 4, T. 29 N., R. 29 E., in 1935. This well attained a depth of 2,800 feet and is reported to have bottomed in granite. Carbon dioxide gas was encountered below 2,300 feet, the total amount developed being reported at about 6,000,000 cubic feet daily from three horizons. All these horizons are probably in the Abo formation of the Lower Permian. It is reported that an analysis of this gas showed 98.6 per cent carbon dioxide, the remainder consisting of nitrogen and a trace of helium.

WILCOX ANTICLINE

The Wilcox anticline is northwest of Estancia in Torrance County. It is a small structure with a reported closure of about 80 feet. The surface rocks consist of the Abo (Permian) formation, which is underlain by the Magdalena formation of Pennsylvanian age. The Magdalena formation rests upon pre-Cambrian rocks.

The first carbon dioxide well on the structure was completed in 1931. Eight wells have been drilled, of which six are now producing carbon dioxide. The initial production of these wells was 230,000 to 800,000 cu. ft. per day, and the average initial pressure was 396 lbs. The carbon dioxide content of the gas is above 98 per cent. The gas is coming from the lower part of the Magdalena formation at depths of 1,250 to 1,500 feet.

Gas from the field is piped 6 miles to the plant of the Witt Gas & Ice Co. at Witt on a branch line of the Atchison, Topeka and Santa Fe Railway serving the Estancia Valley. This plant, originally a 15-ton unit, was completed in 1934 and was the first "Dry-ice" plant to be constructed in New Mexico. It now consists of two 15-ton units and has operated at its capacity of 30 tons daily much of the time during the past two years.

ESTANCIA ANTICLINE

Two wells located a short distance south of the Wilcox anticline encountered noteworthy amounts of carbon dioxide gas in the lower part of the Magdalena formation. The Estancia Co., in 1925-26, drilled a testwell on the Estancia anticline in Sec. 5, T. 6 N., R. 7 E. to a depth of 1,346 feet. Carbon dioxide gas in small amounts was obtained in a 5-foot sand at 1,027 to 1,032 feet. The Wilson, et al, Pace No. 1 well, in Sec. 12, T. 6 N., R. 7 E., was completed in 1928 at a depth of 1,944 feet. Carbon dioxide gas was encountered at several horizons between 1,645 and 1,900 feet. A show of oil was reported in a sand at 1,390 feet. This well is about 5 miles east of the crest of the structure.

BUEYEROS FIELD

The carbon dioxide field in New Mexico that has attracted most interest recently is the Bueyeros field in Harding county. The Bueyeros or Baca anticline is in Tps. 20 and 21 N., Rs. 30 and 31 E. It is approximately 20 miles east of Roy, a station on a branch line of the Chicago, Rock Island & Pacific Railway. This branch line connects with the main line of the Rock Island at

Tucumcari and it intersects the main line of the Santa Fe railway at French. The sedimentary rocks of the general area range from Permian to Recent in age. They include the Abo sandstone and Chupadera formation (Permian), Dockum group (Triassic), Wingate sandstone (Jurassic), Morrison and Purgatoire formations and Dakota sandstone (Cretaceous), and Recent sands and gravels. Some of the higher areas are capped with Tertiary basalt flows.

The surface rocks on the high part of the Bueyeros anticline consist chiefly of the Wingate sandstone and the Dockum group. The Wingate sandstone is the cap rock of three prominent buttes in the area and outcrops in the encircling escarpments. Where it has been removed by erosion the underlying beds of the Dockum group are exposed.

Most of the wells started in the Dockum group but several had the Wingate sandstone as the surface rock. The Dockum group consists of sandstones and shales of prevailing red color. The shallow production is obtained from several sands in the Lower Dockum at depths of 720 to 980 feet, one or more of which may belong to the Santa Rosa sandstone.

Underneath the Dockum group is the Upper Chupadera formation, consisting chiefly of sandstones and shales, and having a thickness of several hundred feet or more. These rocks are underlain by a series of sands and arkose beds which probably belong to the Abo formation. The Magdalena formation (Pennsylvanian) is either absent or quite thin, and the arkose series probably rests directly on pre-Cambrian rocks. The deep production is coming from a sand about 100 feet thick in the Abo and at depths of 1,900 to 2040 feet.

The Bueyeros anticline is an asymmetrical closed structure, the axis trending northwest. The steeper dips are in the western part of the structure. The results of detailed plane table surveys are not available to the writers but the closure is estimated to be more than 300 feet. The high part of the structure appears to be in the southeastern part of T. 21 N., R. 30 E. The wells drilled have proven a productive carbon dioxide gas area approximately 9 miles long and 3 miles wide.

In 1916, the American Producers Corp. drilled a well in the SW. cor. Sec. 32, T. 20 N., R. 31 E., which encountered a flow of carbon dioxide *gas* estimated to be at least 25,000,000 cu. ft. at a depth of 1,955 to 2,055 feet. The well was allowed to flow wide open for more than a year. It bridged itself and ceased flowing and it was plugged and abandoned in April, 1932.

The next drilling in the area was in 1930 when Mr. F. D. Kerns commenced a well in the SE 1/4 NE 1/4 Sec. 34, T. 21 N., R. 30 E. This well was completed in May, 1931, at a depth of 981 feet. An estimated daily production of 3,000,000 cu. ft. was obtained below 940 feet, and water was encountered in the bottom of the hole.

To date nine wells have been drilled in the area of which seven are commercial wells. One well was abandoned due to mechanical difficulties and it may have proved to be a commercial well if completed to the proper horizon. The well of the American Producers Corp., mentioned above, was certainly a commercial well when brought in, even though it has since been plugged. An

offset to this well in Sec. 31, T. 20 N., R. 31 E., has recently been completed at a depth of 2,041 feet, with an estimated flow of over 25,000,000 cu. ft. of carbon dioxide gas and an estimated pressure of over 600 lbs. The producing sand is approximately 100 feet thick.

Of the seven commercial wells, six are producing from the upper horizon and one from the lower. In general, the deeper horizon has proved to be the more prolific and probably the capacity of the shallow wells would be greatly increased by deepening them to the lower horizon. The average initial production of the wells drilled to the shallow producing horizon has been about 3,000,000 cu ft. with an initial pressure of around 400lbs.

The gas present at the Bueyeros anticline is exceptionally high in carbon dioxide content, averaging 99 per cent. Impurities consist of nitrogen and oxygen. The gas is sufficiently pure so that scrubbers and other purifiers are not required prior to its manufacture into "Dry-ice."

Two "Dry-ice" plants have been constructed in the area. The plant of the Western Freezit Corp. is in Sec. 19, T. 20 N., R. 31 E. This is a very small experimental plant and the results obtained to date have not been satisfactory. The New Mexico Carbonic Co. has erected recently a plant in Sec. 34, T. 21 N., R. 30 E. Its capacity is 3 tons a day. If this plant proves to be successful, it is planned to install other units.

Without question, the Bueyeros anticline contains an exceedingly large quantity of carbon dioxide gas. The development of a large-scale carbon dioxide industry at the Bueyeros field will depend on an assured large market for its products, cheap manufacturing costs and efficient distribution. With these problems solved the field should have a promising future.