WV-0012 #2
H.C. Chitwood I 212
Asbestos

UC 149-2

UNION CARBIDE

INTERNAL CORRESPONDENCE

MAY 28 1964 H.C.C.

UNION CARBIDE NUCLEAR COMPANY • RESEARCH CENTER, P. O. BOX 324, TUXEDO, NEW YORK

PLAINTIFF'S EXHIBIT UC-756

To (Name) Dr. Henry Chitwood
Company Technical Center
Location Union Carbide Corporation
Chemicals Division
South Charleston 3, West Virginia

Date May 26, 1964

Originating Dept.

Answering letter date

Subject

Copy to Messrs: J.C. Brantley
G.H. Clewett
S.M. Siegel
C.O. Strother
R.A. Conway

Dear Henry:

Dr. Strother mentioned to me that he had been in contact with you about the discovery that our asbestos could catalyze the oxidation of potassium iodide by atmospheric oxygen. He perhaps also told you of our apparent success in improving the operation of activated sludge sewage plants by the addition of our asbestos. Just after his conversation with you, Dr. Strother asked if I would provide you with the details of our experiments. Since we had not done any significant amount of work on the system, I have held off until we had some tangible data.

The potassium iodide experiments are quite irratic, since they must be conducted in an acid environment under which conditions asbestos is decomposed. Thus, while we did bring about the oxidation of potassium iodide at a rate which was considerably greater than a blank having no asbestos and somewhat greater than a similar run using Quebec asbestos, the curve which was obtained merely reflected the rate of dissolution of the asbestos surface. Chrysotile asbestos, as you may know, is a "laminate" structure having alternate layers of magnesium hydroxide and silica which curl into a tube. The outer surface is magnesium hydroxide. Because of the apparent leaching effect and also because of the sewage treatment success, we changed our experiments to a system which could be conducted in a more favorable pH range for the asbestos and which would have significance to the sewage treatment application.

I have enclosed a description of the work that has been performed on this problem during the last month. Rather than pursue the kinetics and mechanism of any one reaction at this time, we plan to continue to determine the extent of the effect. At the present time we plan to pursue the oxidation of phenolic compounds, the background of which is described in my report. In addition, we intend to investigate the oxidation of glucose both with and without the presence of yeast cultures for the purpose of determining if there might be any application in the fermentation industries. Apparently, oxygen transfer is an important problem in the rapid growth yeast cells.

I would like to invite your comment on this work. You may have some ideas as to the mechanism of this effect or some suggestions as to how to investigate the

Dr. Henry Chitwood: May 26, 1964

effect. Perhaps you have some feel for the possibilities of using asbestos as a high temperature oxidation catalyst. We have often speculated about this, but are not sufficiently familiar with commercial oxidation processes to know if there is any potential here. Unfortunately, asbestos is unstable above about 450°C, at which time it begins to lose its hydroxyl groups. As you might expect, the surface hydroxyl groups are the first to go, hence its catalytic activity may be lost at higher temperatures.

Sincerely yours,

Bill

W. H. Dresher

WHD:AB
Enc.

AERATION CATALYZED BY ASBESTOS May 15, 1964

In April of 1963 it was found that asbestos was an effective catalyst for the oxidation of potassium iodide in aqueous solution by air[1]. During these tests some superiority was noted for Coalinga asbestos products over a standard Quebec product. No further work was done on this effect until it was found, by R.G. Woolery in field work early in 1964, that Coalinga asbestos is extremely effective in accelerating the air oxidation of sewage in activated sludge sewage disposal plants. At this point, work was undertaken to attempt to determine the scope and potential usefulness of asbestos-catalyzed oxidation reactions.

The oxidation of sewage sludge is accomplished by the action of aerobic bacteria which respire oxygen from the water and consume organic matter in their normal metabolic process. The useable portion of this organic matter is converted to cell growth or to carbon dioxide. The remainder constitutes the inactive sewage sludge which, depending upon local conditions, is burned for its fuel value, sold as fertilizer, or just buried. It can be postulated that asbestos assists in this process in one or both of two ways:

1. by assisting in the supply of oxygen to the biological organism.

2. by oxidizing at least some of the organic material directly.

In sewage treatment practice it is common to measure the effectiveness of aeration by measuring the rate of oxidation of sodium sulfite solutions[2]. These measurements are generally made in connection with the measurement of the comparitive effectiveness of various types of mixing and sparging equipment in making oxygen from the air available to the liquid phase. This system was adopted for the comparison of the effectiveness of various asbestos products in enhancing the gas-to-liquid phase transfer of oxygen. For the purpose of these tests, the mixing and sparging equipment were held constant. Tests were performed by stirring a one molar solution of sodium sulfite with a magnetic stirrer while sparging the solution with either air or with other mixtures of oxygen and nitrogen. Asbestos was added to the sodium sulfite solution to make a 0.33 per cent slurry (1 gram of asbestos in 300 ml. solution). Since H^+ is a product of the oxidation the solution was buffered with NaAc and HAc at the desired pH. At periodic intervals an aliquot was removed from the system and titrated with standardized iodine solution in order to determine the amount of unoxidized sodium sulfite still remaining in the system. In every test, as is the experience in the sewage treatment industry tests, the rate of oxidation of sodium sulfite was independent of the concentration of $SO_3^=$ and of the resultant $SO_4^=$ and was linear. Figure 1 shows a comparison of the rates of oxidation of sodium sulfite when no asbestos was added, Quebec Grade 7R3 asbestos was added, and when three Coalinga products were added - dry mechanically processed (L-1), wet mechanically processed (CMS), and wet chemically processed (SAD). The Quebec asbestos sample enhanced the oxidation rate by a factor of approximately two. Coalinga products enhanced the oxidation rate between three and four times greater than the blank. As might be predicted, the relative order of increases in oxidation rate was directly proportional to the severity of the treatment to

(1) Progress Report, W.H. Dresher, April 15, 1963.

(2) "Biological Treatment of Sewage and Industrial Waster," 185, Reinhold Publishing Co., N.Y. (1956).

which the asbestos had been subjected during its refining. Figure 2 shows the effect of pH on the oxidation. Between pH 6 and 8 there seems to be little or no change in the oxidation rate with pH. Below pH 6 the rate is slightly increased over that at higher pH values. Figure 3 shows the rate curves obtained at various oxygen partial pressures, and Figure 4 shows the effect of the partial pressure of oxygen on the oxidation rate.

While no experimental work has been performed on the second mechanism postulated, Dr. S. M.Siegel, of the Union Carbide Research Institute, has studied the role of silicate minerals, among which was chrysotile asbestos, in the oxidation and polymerization of lignin precursors. He has found that the lignin-forming reaction, normally accomplished by enzymatic reaction, can be catalyzed by chrysotile asbestos even in the absence of enzyme. The use of chrysotile asbestos resulted in a tenfold increase of polymer over a blank in which no asbestos was used(3). Based on these findings, it seems reasonable to expect at least some portion of the oxidation of the sewage to be accomplished directly by the asbestos. In addition, Dr. Siegel found that orthodiphenol compounds could be oxidized in preference to other phenol compounds. This work of Dr. Siegel helps to explain some work conducted in this laboratory in July of 1962(4) wherein, during a search for inexpensive organic dispersing reagents for chrysotile asbestos, it was found that the o-phenol compounds catechol, pyrogallol, gallic acid, and digallic acid, were capable of dispersing asbestos in alkaline pH regions but only after the slurry had undergone a series of color changes. Other phenols, such as resorcinol, which did not contain ortho-hydroxyl groups were ineffective and did not cause a color change. Based upon Dr. Siegel's work, the color change ranging from brown-green to black, was the oxidation product of the phenol compound.

Further work should be done in determining the types of oxidation reactions which are possible due to the presence of asbestos and attempts made to find additional industrial applications of this property of asbestos. Potential applications might be found in the fermentation industries - beverages, drugs, and chemicals, for example.

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(3) S.Siegel, Proc. Nat. Acad. Sci. U.S. 43, 811 (1957).

(4) W.H.Dresher, Notebook No. 294, pages 46 to 49 inclusive.

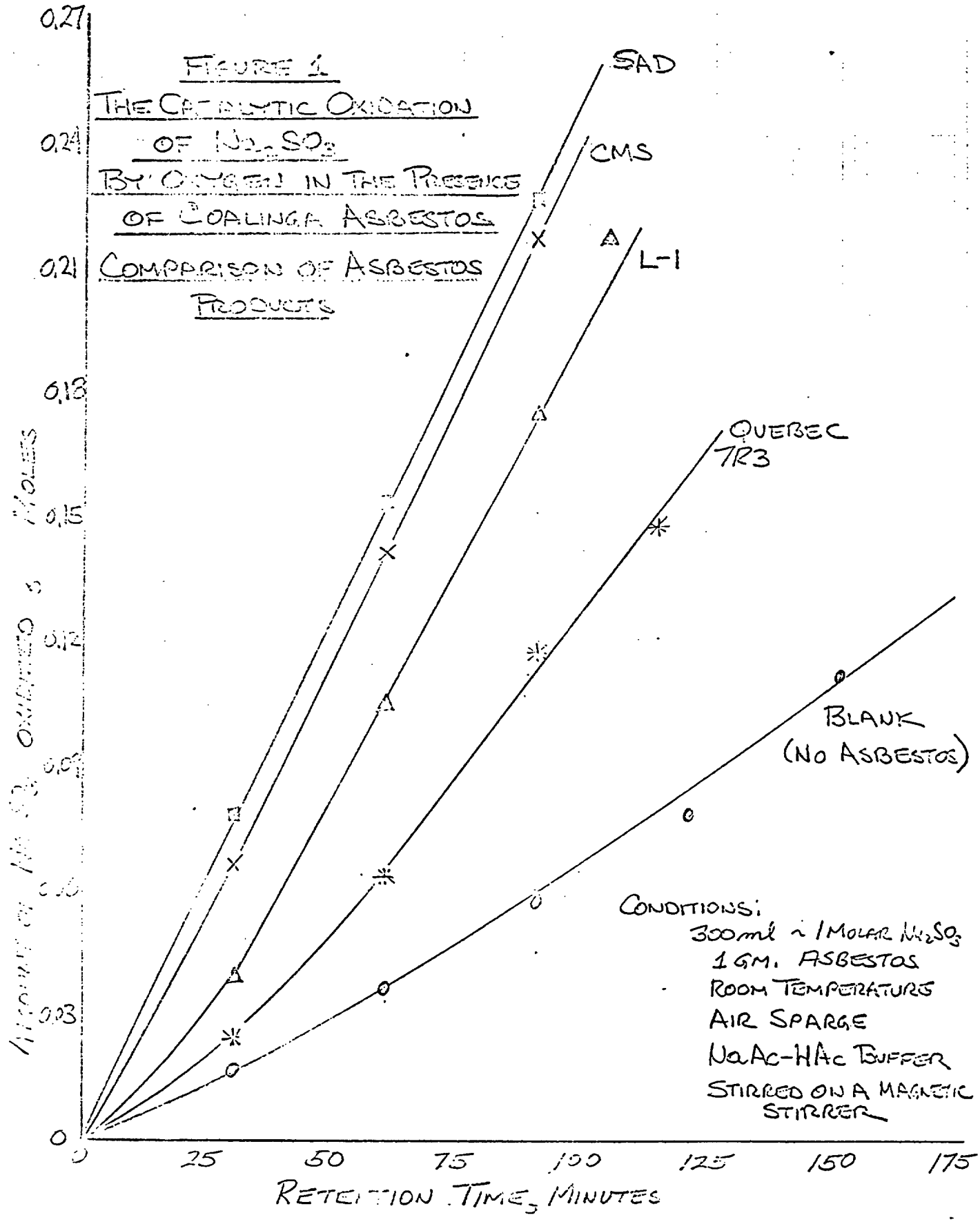
FIGURE 1
THE CATALYTIC OXIDATION OF Na_2SO_3 BY OXYGEN IN THE PRESENCE OF COALINGA ASBESTOS
COMPARISON OF ASBESTOS PRODUCTS
SAD
CMS
L-1
QUEBEC 7R3
BLANK (NO ASBESTOS)
0.27
0.24
0.21
0.18
0.15
0.12
0.09
0.06
0.03
0
MOLES Na_2SO_3 OXIDIZED
25
50
75
100
125
150
175
RETENTION TIME, MINUTES
CONDITIONS:
300ml ~ 1 MOLAR Na_2SO_3
1 GM. ASBESTOS
ROOM TEMPERATURE
AIR SPARGE
NaAc-HAc BUFFER
STIRRED ON A MAGNETIC STIRRER

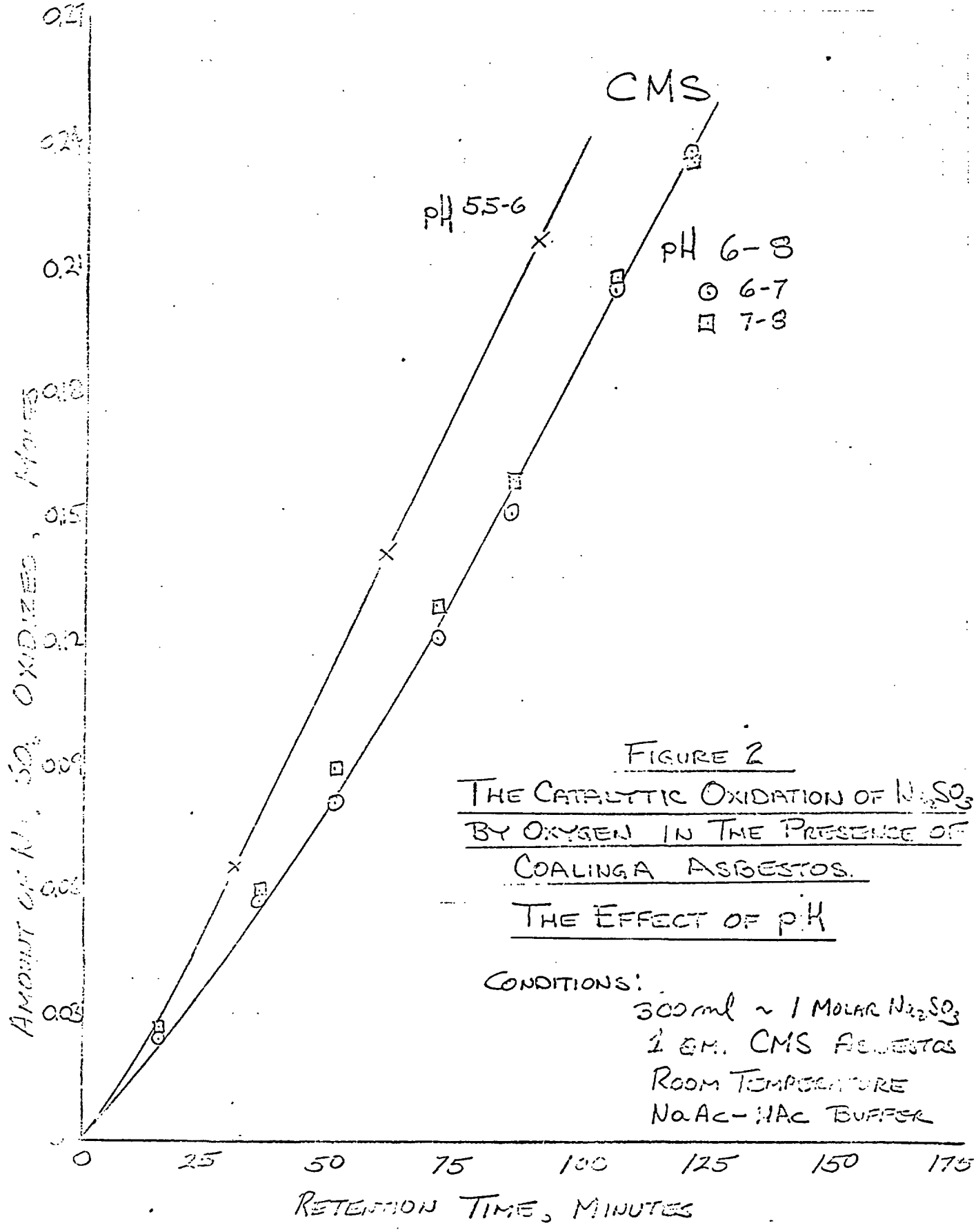

FIGURE 2

THE CATALYTIC OXIDATION OF N_2SO_3 BY OXYGEN IN THE PRESENCE OF COALINGA ASBESTOS.

THE EFFECT OF pH

CONDITIONS:

300 ml ~ 1 MOLAR N_2SO_3
1 GM. CMS ASBESTOS
ROOM TEMPERATURE
NaAc-HAc BUFFER

C. M. Neumann May 19, 1964

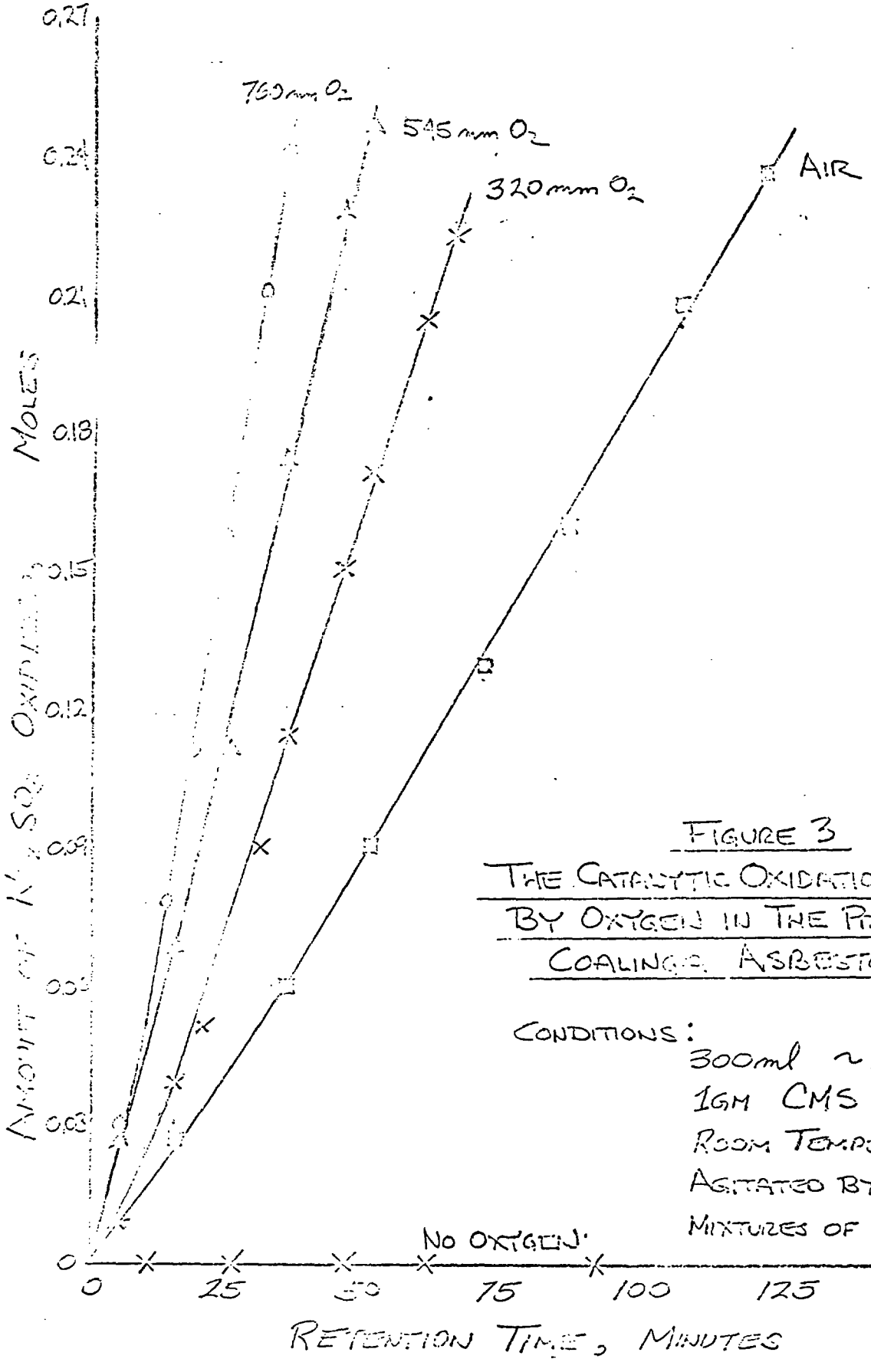

FIGURE 3

THE CATALYTIC OXIDATION OF Na_2SO_3 BY OXYGEN IN THE PRESENCE OF COALINGA ASBESTOS

CONDITIONS:
300ml ~1 MOLAR Na_2SO_3
1GM CMS ASBESTOS.
ROOM TEMPERATURE
AGITATED BY MAGNETIC STIR
MIXTURES OF O_2 & N_2 SPARG

A. H. Baumann May 19,.