

ADVANCES IN SODA LIME TECHNOLOGY

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Introduction

The absorption of carbon dioxide in self contained breathing apparatus plays a vital role in respiratory protection. However, as the requirements of breathing equipment become more exacting the performance of the CO₂ absorbent becomes increasingly more critical.

This paper discusses advances in soda lime canister efficiency by consideration of the physical factors involved and looks ahead to possible ways of overcoming the current inherent reaction limitations.

1. Soda Lime

The ability of soda lime to react with a number of gases was documented in the early part of the twentieth century⁽¹⁾. With the advent of the Second World War soda lime became a standard constituent of filter masks for respiratory protection.

Since these early days soda lime has become an established CO₂ absorbent for such applications as anesthesiology and closed circuit breathing apparatus.

Soda lime is essentially a mixture of caustic soda (NaOH) and lime (Ca(OH)₂), although modern formulations may also contain potassium hydroxide (KOH).

It is postulated that this mixture is synergistic in nature and this feeling was suitably expressed by R. Hum⁽²⁾ in 1948.

Soda Lime is made by slaking quicklime with sodium hydroxide solution. The mixture of two hydroxides, so formed, is valuable not only because, unlike caustic soda, it is neither deliquescent nor easily fusible, but also from the fact that, for some reason, it is more active chemically than either of its constituents.

2. Uses Of Soda Lime

Soda lime is used in a wide variety of industries incorporating health care, the industrial environment and also military applications. An approximate breakdown of the soda lime market for North America (USA and Canada) is given in Figure 1.

Anesthesiology still commands, as it has done historically, the largest single market share. However, respiratory protection, covering both the safety industry and the armed forces, is an increasing market area.

The requirements of soda lime for these latter applications, where high respiratory function and even panic may be observed, differ markedly from products used in anesthesiology where the patient is in a controlled condition of low respiratory rate. One must, therefore, question whether an anesthetic grade soda lime, developed for an application with such a large built-in safety margin, is likely to satisfy all the criteria of a critical life support application.

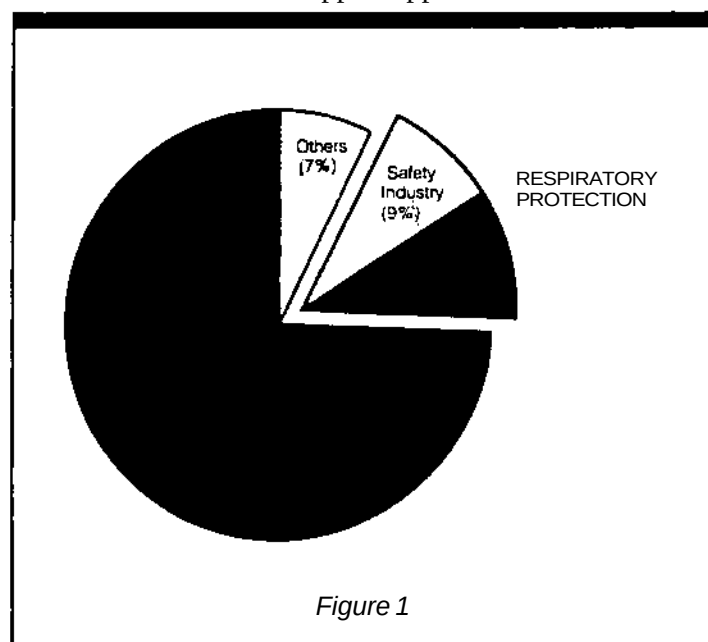


Figure 1

3. Use Of Soda Lime In Respiratory Protection

Having, albeit briefly, considered the relative requirements for soda lime in anesthetic and respiratory protection applications, it is interesting to draw up a list of performance criteria for individual breathing apparatus.

FIRE FIGHTING	Long Duration
DIVING	Cold temperature (North Sea)
	Long duration (Military)
	Short duration (Bale-out sets)
MINING Rescue	Long duration
Escape	Short duration
	ergonomics (belt worn devices)
ESCAPE HOODS	Short duration
	High temperature
	High respiratory rate
	Semi and passive absorption

SODA LIME PERFORMANCE CRITERIA FOR BREATHING APPARATUS

It is clearly evident that no one set of common parameters can fulfill all of the breathing apparatus requirements.

The optimum performance parameters for each specific apparatus should be jointly developed relative to the end use conditions.

4. Limitations Of Soda Lime System

4.1 SODA LIME - CO₂ REACTION

When considering the reaction between soda lime and CO₂ five basic factors must be taken into consideration.

- Diffusion of CO₂ to aqueous layer surrounding granule
- Reaction at aqueous layer
 $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$
- $\text{H}_2\text{CO}_3 + 2\text{NaOH} = \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$
- Double decomposition reaction
 $\text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 = \text{CaCO}_3 + 2\text{NaOH}$
- Formation of insoluble carbonates from (iv)

Given that a typical composition of soda lime is: (exact compositions will vary from one manufacturer to another, and is dependent on final moisture content)

Calcium Hydroxide	Ca(OH)_2	73.0%
Sodium and/or Potassium Hydroxide	NaOH/(KOH)	3.0%
Carbonate		4.0%
Inerts		3.0%
Water		17.0%

It can be calculated that the theoretical soda lime absorption of CO₂ is approximately 460g CO₂/kg or 230 litres CO₂ (at s.t.p.)/kg. In most practical situations absorption capacities of about 250g CO₂/kg soda lime

are common, while in some cases activities in excess of 300g/kg are encountered. These quite respectable soda lime performances still fall far below the theoretical maximum.

4.2 LIMITING FACTORS

Investigations by a number of workers (3), (4), (5) have concluded that the overall soda lime-CO₂ reaction is physically controlled. The carbon dioxide molecules cannot penetrate into the center of the soda lime leaving each granule with an **unreacted** core. This mechanism is sometimes referred to as diffusion control and is the major factor in the under performance of soda lime filter beds. The exact cause of this diffusion limitation is still to be resolved, current postulates include:

- Sealing of the soda lime surface by carbonate formation (pore mouth poisoning)
- Premature dehydration of the soda lime, that is, insufficient aqueous interface to allow required mass transfer.
- Saturation of pores on soda lime surface with water from reaction with CO₂

5. Optimization Of Current Product

Although the inherent limitations of the soda lime-CO₂ system are significant, steps can be investigated to optimize the absorption capacity of the soda lime bed and improve canister duration. A useful representation of the controlling reaction processes is given in Figure 2.

The effect of changing simple practical parameters (such as flow rate, concentration and particle size) can be quickly assessed, the aim being to achieve a situation where the diffusion limitation of the soda lime is minimized, allowing all the available hydroxide to react with carbon dioxide (chemical rate controlled).

Two of the main factors affecting the overall soda lime bed efficiency are residence time (space velocity) and particle size. In order to maximize the soda lime's absorption capacity, the smallest possible particle size should be used in conjunction with the longest practical residence time. Recent investigations carried out by the Experimental Diving Unit of the United States Navy⁽⁶⁾ have shown that by simply reducing the particle size from a 4-8 mesh to an 8-12 mesh the duration of the soda lime canister can be doubled, without giving rise to an unacceptable breathing resistance. The importance of designing CO₂ scrubbers around the concept of minimum residence times to allow sufficient gas/solid contact has been known for some time and cannot be overstated.

SYSTEM DIAGNOSIS

Plot size function a against observed rate against constant K_0

$$\text{Where } a = \frac{d}{P_t d_p^2}$$

e = Fractional bed voidage

P_t = Total system pressure (atm)

d_p = Particle diameter (cm)

$$K_0 = \frac{(P_{A_i} - P_{A_e})}{(P_{A_i} - P_{A_e})} \frac{2 S f_r}{P_t M}$$

Where P_{A_i} = Inlet partial pressure A (atm)

P_{A_e} = Exit partial pressure A (atm)

S = Space velocity ($\text{cm}^3 \text{ feed at } 25^\circ\text{C} / (\text{cm}^3 \text{ adsorbent}) (\text{hr})$)

f_r = Gas density (g/cm^3)

M = Molecular wt gas (g)

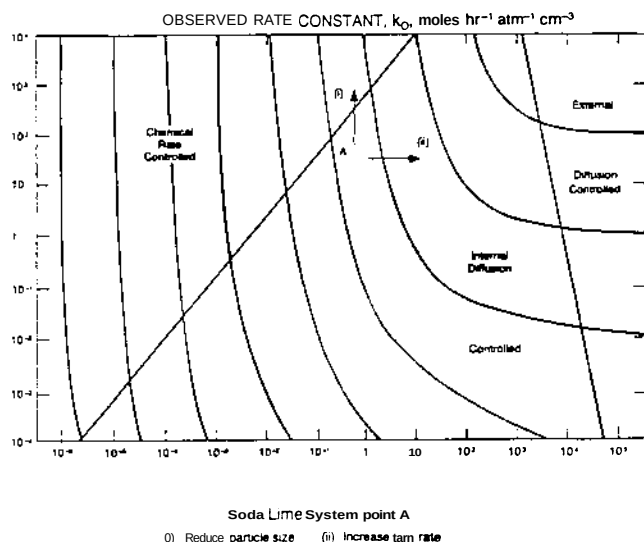


Figure 2

6. Investigation Of Advanced Soda Lime Systems

Optimization of the existing soda lime system by improving mass transfer, through an increase in geometric surface (decrease in particle size) and elongation of residence time, does not tackle the inherent soda lime problem of diffusion limitation.

In order to overcome this physical control, changes in the intrinsic surface structure are required, this means primarily looking at the porosity of the product.

Earlier work (7), summarized in Figure 3, has shown there is a strong correlation between the method of manufacture and resultant soda lime porosity. Currently all commercial soda limes are manufactured by the 'wet' method (sometimes referred to as dough or paste method). When producing soda lime it is important to maintain a balance between the product's porosity (and adsorption properties) and granular mechanical strength, too high a porosity gives low bulk density and poor abrasion resistance.

Materials manufactured by the wet method are subjected to a moderate temperature drying stage ($<140^\circ\text{C}$) which is insufficient to produce any hardening by mixed oxide linkage or calcining. The restrictive nature of the wet method's manufacturing variables make it unattractive as a means of producing materials of diverse surface characteristics.

SODA LIME ORIGIN	MERCURY PORE cm^3/g	SURFACE AREA m^2/g	ABRASION RESISTANCE %	CO ₂ ABSORPTION CAPACITY (gCO_2/kg)		
				THEORETICAL	Static	Dynamic
UK	0.30	15	0.52	455	408	274
WEST GERMANY (1)	0.34	9	0.83	475	402	206
WEST GERMANY (2)	0.35	19	1.11	414	387	270

PHYSICAL PROPERTIES OF PROPRIETARY SODA LIME PRODUCTS

K Stoessel, Thesis, Zurich 3689 (1965)

Figure 3

Extensive experimental work at MP united Drug[®] has resulted in the development of an alternative route for the preparation of mixed metal hydroxide absorbents, Figure 4. The precipitation of the hydroxides in the presence of a modifying agent, and subsequent treatment of the resultant gel provide sufficient scope for the preparation of soda lime with different surface properties.

6.1 SURFACE CHARACTERISTICS

The techniques used to analyze the surface properties of the soda lime materials are identified in Figure 5.

The specific surface area was determined by means of nitrogen monolayer absorption, using techniques based on the work of Brunauer, Emmett and Teller[®]. All samples were preconditioned at 120°C.

A measure of pore volume was also derived from the adsorption of nitrogen, the smaller pores being filled first, with the larger pores (up to 300 Å radius)

being filled as the equilibrium pressure is approached.

The pore volume, measured by means of mercury intrusion, works in a converse manner with the bigger pores being filled first, while the smaller ones (down to 37 Å radius) are only filled at higher pressure (up to 2000 kg/cm²).

The results of surface characterization experiments of differing soda lime grades are given in Figures 6, 7 and 8.

Figure 6 shows a standard soda lime grade produced by the wet method of manufacture. Its pore size distribution is dominated by pores of radius 300 - 800 Å.

The results obtained for commercial grades of soda lime agree with those reported earlier.

LP101 (Figure 7), an experimental sample, shows clearly that the inclusion of a modifying agent and subsequent treatment can dramatically affect the surface properties. An increase in surface area and total pore volume were noted, the pore distribution shifting towards the smaller size (<100 Å).

In the preparation of LP106 (Figure 8) the ratio of modifying agent to active hydroxide was different to LP101. The high BET surface area is due in part to the large number of small pores (N₂ porosity not shown graphically in Figure 8). The total porosity is approximately five times that of standard soda lime.

It is postulated that by utilizing these new production techniques materials can be produced that will have two distinct advantages over existing soda lime products, namely

- More efficient absorption of carbon dioxide
- Increased resistance to dust formation

Work is currently ongoing in an effort to substantiate these beliefs. Obviously the practical consequence of this work is the development of soda lime material that will enable engineers more flexibility which designing new breathing apparatus.

MPUD DEVELOPMENT PROGRAMME

Experimental Work

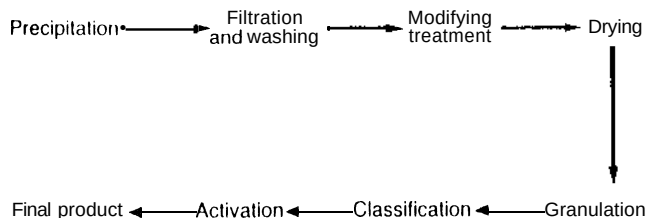


Figure 4

SURFACE CHARACTERISATION

Surface Area Determination

Method

Nitrogen Monolayer BET

Typical Results

Soda Lime	: 10 - 20 m ² /g
Alumina	: 300 m ² /g
Activated Carbon	: 1000 m ² /g

Porosity Measurements

Nitrogen Absorption

Pores up to 300 Å radius

Mercury Intrusion

Pores from 37 Å radius

Figure 5

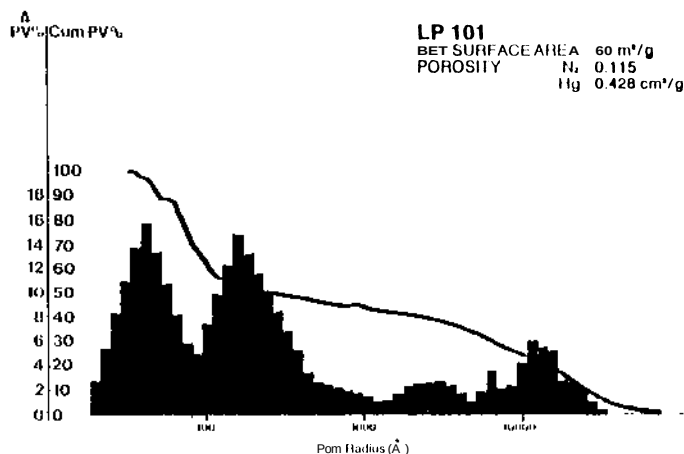


Figure 6

7. Future Requirements

Any improvements in the ability of soda lime to absorb CO_2 that can be achieved are particularly useful when one considers the diverse nature of current developments in respiratory protection.

DIVING SYSTEMS

A CO_2 absorbent with enhanced performance under conditions of cold water and high pressure is desirable, particularly for bale-out sets. The nature of soda lime deactivation under these conditions is thought to be chemical rather than physical (10) and further product modification may be required.

SMOKE HOODS

Interest in this type of respiratory protection device has been steadily increasing. There appear to be two generalized approaches, both of which require specialized absorbent packages.

FILTER HOODS:

Absorbent is required to remove carbon dioxide produced by combustion process and possible upstream oxidation of carbon monoxide. It would be desirable to have soda lime in a configuration where it was not prematurely dehydrated by high incident temperatures.

BREATHABLE GAS HOODS:

In these type of hoods or apparatus that incorporate a large dead space, the design criteria of major influence is one of projected surface area. Thus the rate of removal is optimized to reduce any buildup of CO_2 .

GENERAL BREATHING APPARATUS

In this area the possible advancement as a result of increase soda lime performance are likely to be less dramatic. However, the following beneficial consequences may arise

- More even canister performance over a range of operating conditions
- Reduction in the tendency to form dust
- Evolution of new particle geometries

8. Summary

1. Select the optimum grade of Soda Lime for your individual requirement. (All Soda Limes are not the same.)
2. If developing a new product consult the chemical manufacturer at an early stage to ensure maximum performance.
3. Advancements in Soda Lime technology would seem to offer a solution to Soda Lime's inherent restriction of diffusion limitation.
4. Using new techniques, the chemical manufacturer may be able to offer alternative CO_2 absorption packages to current, traditional granular types.

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