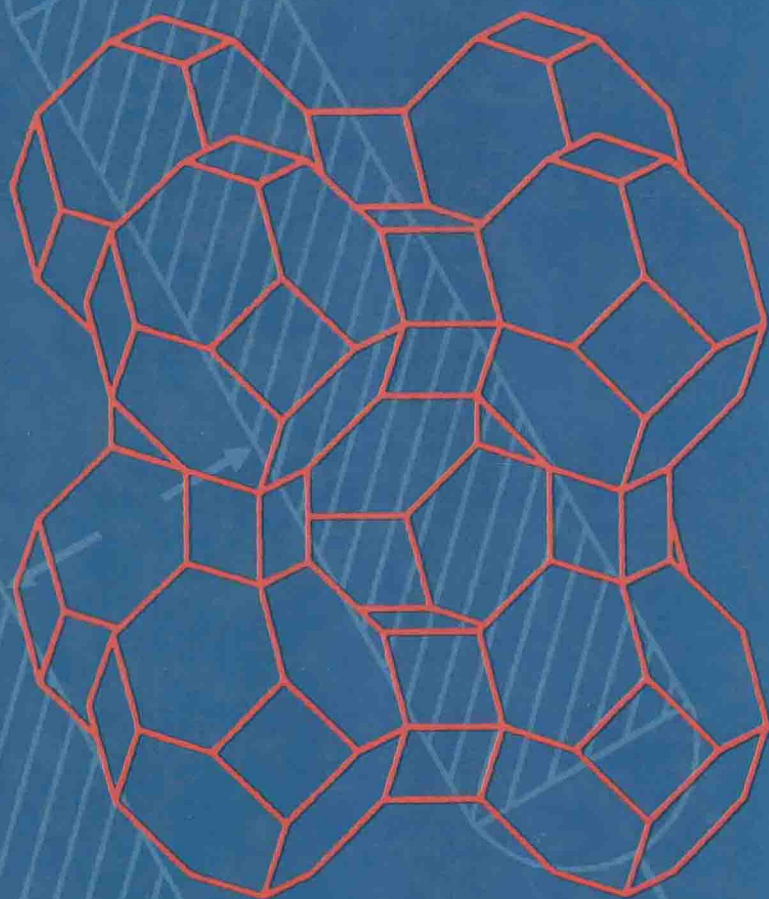


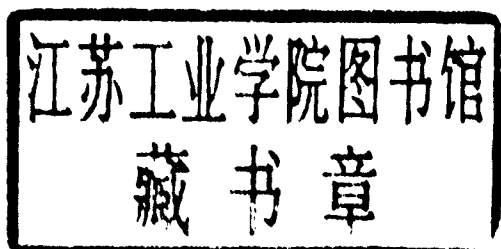
Adsorption Technology & Design



**Barry Crittenden &
W John Thomas**

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W. John Thomas and Barry Crittenden



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Adsorption Technology and Design

Foreword

When asked about the most important technology for the Process Industries, most people might offer 'reaction'. If one considers where value is really added, it is more probably in the separation and purification of the products. It is therefore a great pleasure to find that Professors Crittenden and Thomas have made a major contribution to this with their new book. My career has been spent in the Industrial Gases industry where cost-effectiveness of separation processes is the main way of creating competitive advantage. In the last few years, adsorption technology has become increasingly important in market development and market share. It has allowed on-site gas generation, with considerable price reduction, where previously we would have supplied liquefied gases. This increased commercialization of the technology stimulates further research into both the adsorbates and their applications, the virtuous circle.

In *Adsorption Technology and Design*, we find a carefully crafted blend of theory, practice and example. The reader who seeks only an overview is as well served as the experienced practitioners seeking to broaden their knowledge. Chapters 1 and 2 are an introduction that allows the non-practitioner to gain some understanding of the history and technology. Chapters 3 and 4 deal with the theory of adsorption equilibria and adsorption kinetics respectively. These well-structured chapters define the basic science of the subject and provide the essential grounding necessary to allow applications development. Chapters 5 and 6 are a comprehensive description of processes and cycles and their design procedures. Here the practitioner may gain experience or inspiration to innovate. These chapters are suitable reading for both the novice and the expert. Chapter 7 is the consolidation of the book. Here we see how theory is put into commercial practice. It also clearly illustrates the variety of possible approaches to particular processes and the rate of development of the technology. Finally

in Chapter 8 we have a review of available literature that is free from criticism or comment.

I have no doubt that this book is a significant milestone for the subject and that it will enjoy the success it deserves.

Professor Keith Guy, FEng, FICHEME

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1

The development of adsorption technology

1.1 INTRODUCTION

The ability of some solids to remove colour from solutions containing dyes has been known for over a century. Similarly, air contaminated with unpleasant odours could be rendered odourless by passage of the air through a vessel containing charcoal. Although such phenomena were not well understood prior to the early twentieth century, they represent the dawning of adsorption technology which has survived as a means of purifying and separating both gases and liquids to the present day. Indeed, the subject is continually advancing as new and improved applications occur in competition with other well-established process technologies, such as distillation and absorption.

Attempts at understanding how solutions containing dyes could be bleached, or how obnoxious smells could be removed from air streams, led to quantitative measurements of the concentration of adsorbable components in gases and liquids before and after treatment with the solid used for such purposes. The classical experiments of several scientists including Brunauer, Emmett and Teller, McBain and Bakr, Langmuir, and later by Barrer, all in the early part of the twentieth century, shed light on the manner in which solids removed contaminants from gases and liquids. As a result of these important original studies, quantitative theories emerged

2 The development of adsorption technology

which have withstood the test of time. It became clear, for example, that the observed effects were best achieved with porous solids and that adsorption is the result of interactive forces of physical attraction between the surface of porous solids and component molecules being removed from the bulk phase. Thus adsorption is the accumulation of concentration at a surface (as opposed to absorption which is the accumulation of concentration within the bulk of a solid or liquid).

The kinetic theory of gases, developed quantitatively and independently by both Maxwell and Boltzmann in the nineteenth century, with further developments in the early part of the twentieth century by Knudsen, reveals that the mass of a gas striking unit area of available surface per unit time is $p(M/2\pi R_g T)^{1/2}$, where p is the gas pressure and M is its molecular mass. As discussed later (Chapter 4), according to the kinetic theory of gases the rate of adsorption of nitrogen at ambient temperature and 6 bar pressure is $2 \times 10^4 \text{ kg m}^{-2}\text{s}^{-1}$. At atmospheric pressure this would translate to $0.33 \times 10^4 \text{ kg m}^{-2}\text{s}^{-1}$. Ostensibly then, rates of adsorption are extremely rapid. Even accounting for the fact that adsorbate molecules require an energy somewhat greater than their heat of liquefaction (q.v. Chapter 3) the above quoted rates would only be reduced by a factor $\exp(-E_a/R_g T)$: if E_a , the energy required for adsorption, were 10 kJ mol^{-1} at ambient temperature and pressure, the rate of adsorption would be $4.5 \times 10^2 \text{ kg m}^{-2}\text{s}^{-1}$. However, observed rates are less than this by a factor of at least 10^{-10} for several reasons, principally the resistance offered by mass transfer from the bulk fluid to the surface of the porous solid and intraparticle diffusion through the porous structure of the adsorbent. Such transport resistances are discussed more fully in Chapter 4.

Industrial applications of adsorbents became common practice following the widespread use of charcoal for decolourizing liquids and, in particular, its use in gas masks during the 1914–18 World War for the protection of military personnel from poisonous gases. Adsorbents for the drying of gases and vapours included alumina, bauxite and silica gel; bone char and other carbons were used for sugar refining and the refining of some oils, fats and waxes; activated charcoal was employed for the recovery of solvents, the elimination of odours and the purification of air and industrial gases; fuller's earth and magnesia were found to be active in adsorbing contaminants of petroleum fractions and oils, fats and waxes; base exchanging silicates were used for water treatment while some chars were capable of recovering precious metals. Finally, some activated carbons were used in medical applications to eliminate bacteria and other toxins. Equipment for such tasks included both batch and continuous flow configurations, the important consideration for the design of which was to ensure adequate contact between adsorbent and fluid containing the component to be removed (the adsorbate).

1.2 EARLY COMMERCIAL PRACTICE

Full details of early commercial practice can be found in the writings of Mantell (1951). The oil industry used naturally occurring clays to refine oils and fats as long ago as the birth of that industry in the early part of the twentieth century. Clay minerals for removing grease from woollen materials (known as the practice of fulling) were used extensively. The mineral came to be known as fuller's earth. Its composition consists chiefly of silica with lower amounts of alumina, ferric oxide and potassium (analysed as the oxide). Other naturally occurring clays (kaolin and bentonite) also contain large proportions of silica with smaller proportions of alumina and were also used for bleaching oils and petroleum spirits. Two methods were in common use for decolouring oil and petroleum products: the oil could be percolated through a bed of granular clay or it could be directly contacted and agitated with the clay mineral. The oil or lubricant to be bleached was first treated with sulphuric acid and a little clay, filtered and subsequently run into mixing agitators containing the adsorbent clay and which decolourized the lubricant after a sufficiently long contact time (of the order of one to three minutes) and at a suitable temperature (usually about 60–65°C).

Another mineral, which was widely used as a drying agent, was refined bauxite which consists of hydrated aluminium oxide. It was also used for decolourizing residual oil stocks. Another form of aluminium oxide mineral is florite which adsorbs water rapidly and does not swell or disintegrate in water. Consequently, it was, and still is, used for the drying of gases and organic liquids. The early practice was to utilize beds of florite at room temperature through which was pumped the organic liquid containing moisture. Reactivation of the bed was accomplished by applying a vacuum and heating by means of steam coils located within the bed. Alternatively, the beds were reactivated by circulating an inert gas through the adsorbent, the desorbed water being condensed on emergence from the bed in cooled receptacles.

Some types of carbon were in common use for decolourizing and removing odours from a wide variety of materials. Carbons were also used for treating water supplies. The decolourization of liquids, including the refining of sugar melts, was accomplished by mixing the carbon adsorbent with the liquid to be bleached and subsequently filtering. In some cases the residual adsorbent was regenerated for further use by passing steam through a bed of the spent adsorbent. In the case of water treatment, non-potable waters were either percolated through beds of carbonaceous adsorbent, or activated carbon was added to water in mixing tanks. The resulting effluent was then treated with chlorine to remove toxins. Alternatively, the contaminated water was first treated with excess chlorine and then allowed

to percolate through a carbon bed. The method of water treatment depended on both the extent and form of contamination. The spent carbonaceous adsorbents were usually regenerated by steaming in a secondary plant. Activated carbons were in general use during the first three decades of the twentieth century for the purification of air and for recovering solvents from vapour streams. The carbon adsorbents were activated prior to use as an adsorbent by treatment with hot air, carbon dioxide or steam. The plants for solvent recovery and air purification were among the first to employ multibed arrangements which enabled regeneration of the carbon adsorbent (usually by means of hot air or steam) while other beds were operating as adsorbers. Thus the concept of cyclic operation began to be adopted and applied to other operations on a broader basis.

The dehumidification of moisture-laden air and the dehydration of gases were, and still are, achieved by means of silica gel as an adsorbent. In 1927, for example, an adsorption unit containing silica gel was installed to dehumidify iron blast furnace gases at a factory near Glasgow. It has been pointed out (Wolochow 1942) that this plant was the first known plant using a solid adsorbent for dehumidifying blast furnace gases. Six silica gel units treated one million cubic metres of air per second. Five of the units acted as adsorbers while the sixth unit was being regenerated. An arrangement of piping and valves enabled each adsorber to be switched sequentially into use as an adsorber, thus providing for a continuous flow of dehumidified gas. This unit is an example of one of the earlier thermal swing processes in operation.

1.3 MODERN PRACTICE

Thermal swing adsorption (TSA) processes gradually became dominant for a variety of purposes by the end of the first quarter of the twentieth century. But it was not until the advent of adsorbents possessing molecular sieving properties when processes for the separation of gaseous mixtures developed. Naturally occurring and synthesized alumina-silica minerals (discussed in Chapter 2) have unique crystalline structures, the microporosity of which is precisely determined by the configuration of silica-alumina cages linked by four- or six-membered oxygen rings. Such structures admit and retain molecules of certain dimensions to the exclusion of others, and are therefore excellent separating agents. Barrer (1978) extensively researched and reviewed the adsorptive properties of these materials which are referred to as zeolites. Walker *et al.* (1966a, 1966b), on the other hand, thoroughly investigated the adsorptive properties of microporous carbons and laid many of the foundations for the development

of molecular sieve carbons, which are less hydrophilic than zeolites, and can therefore separate wet gaseous streams effectively.

Although the development of a whole range of laboratory synthetic zeolites, stimulated by the researches of Barrer, precipitated a rapid growth in commercial pressure swing adsorption (PSA) processes (a selection of which are described in Chapter 7), as a historical note it should be stated that the first patents filed for such processes were due to Finlayson and Sharp (1932) and Hasche and Dargan (1931). More than two decades elapsed before two commercial processes for the separation of air, patented by Guerin de Montgareuil and Domine (1964) and Skarstrom (1958), became the foundation for pressure swing adsorption separation techniques on a commercial scale. The essential difference between the earlier thermal swing processes (TSA), and the pressure swing process (PSA) is in the method by which the adsorbent is regenerated following adsorption of the most strongly adsorbed component of a gaseous or liquid mixture. Increase in temperature of the adsorbent bed is the driving force for desorption in TSA processes whereas reduction in total pressure enables desorption in PSA processes. The rapid growth in the number of patents for PSA processes shown in Figure 1.1 is testimony to the successful commercialization of these processes. Their prominence is due principally to the much shorter cycle times required for the PSA technique than TSA methods. Thermal swing processes require cycle times of the order of hours on account of the large thermal capacities of beds of adsorbent. Reduction in pressure to achieve desorption may, on the other hand, be accomplished in minutes rather than hours. Not all TSA processes can, however, be simply transposed into PSA processes solely because of the difference in adsorbent bed regeneration times. TSA processes are often a good choice when components of a mixture are strongly adsorbed, and when a relatively small change in temperature produces a large extent of desorption of the strongly adsorbed species. PSA processes are more often adopted when a weakly adsorbed component is required at high purity: furthermore, cycle times are much shorter than in TSA processes and therefore greater throughputs are possible utilizing PSA techniques.

TSA and PSA processes are, by virtue of the distinct adsorption and regeneration components of the cycle, not continuous processes, although a continuous flow of product may be achieved by careful design and bed utilization. Moving bed and simulated moving bed processes are, however, by their very nature truly continuous. Examples of these are given in Chapter 7, but here it suffices to say that a number of continuous commercial processes for the separation of aromatic mixtures, the separation of n-paraffins from branched and cycloalkanes, the production of olefins from olefin and paraffin mixtures and the isolation of fructose from corn syrup, have been in operation since the early 1980s.

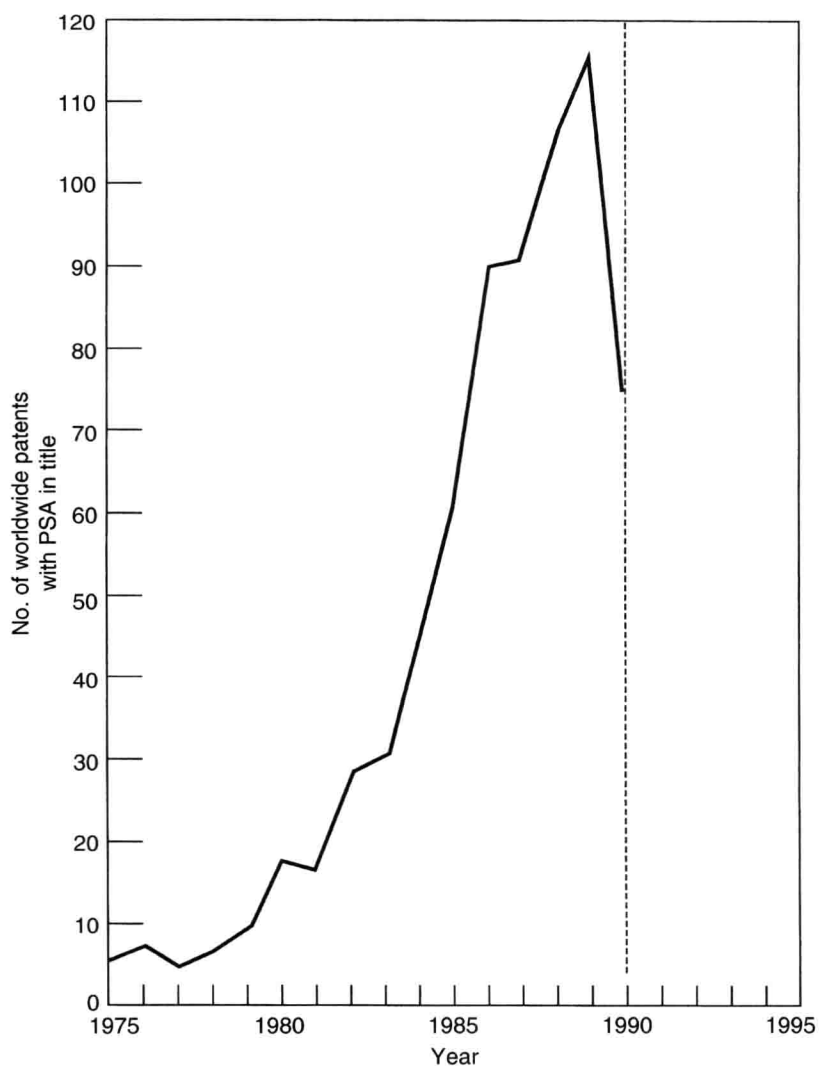


Figure 1.1 Growth of patents relating to PSA processes (adopted from Sircar, 1991).

Until relatively recently, chromatographic processes have been confined to the laboratory for purposes of the analysis of gaseous and liquid mixtures. The pharmaceutical industry has also utilized the principles of chromatography for preparing batches of pharmaceutical products. Elf-

Aquitaine, however, operate a large-scale commercial chromatographic process for the separation of n- and i-paraffins from light naphtha feeds and this is briefly described in Section 7.8.

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2

Adsorbents

To be technically effective in a commercial separation process, whether this be a bulk separation or a purification, an adsorbent material must have a high internal volume which is accessible to the components being removed from the fluid. Such a highly porous solid may be carbonaceous or inorganic in nature, synthetic or naturally occurring, and in certain circumstances may have true molecular sieving properties. The adsorbent must also have good mechanical properties such as strength and resistance to attrition and it must have good kinetic properties, that is, it must be capable of transferring adsorbing molecules rapidly to the adsorption sites. In most applications the adsorbent must be regenerated after use and therefore it is desirable that regeneration can be carried out efficiently and without damage to mechanical and adsorptive properties. The raw materials and methods for producing adsorbents must ultimately be inexpensive for adsorption to compete successfully on economic grounds with alternative separation processes.

The high internal surface area of an adsorbent creates the high capacity needed for a successful separation or purification process. Adsorbents can be made with internal surface areas which range from about $100 \text{ m}^2/\text{g}$ to over $3000 \text{ m}^2/\text{g}$. For practical applications, however, the range is normally restricted to about $300\text{--}1200 \text{ m}^2/\text{g}$. For most adsorbents the internal surface area is created from pores of various size. The structure of an adsorbent is shown in idealized form in Figure 2.1. Many adsorbent materials, such as carbons, silica gels and aluminas, are amorphous and contain complex networks of interconnected micropores, mesopores and macropores. In contrast, in zeolitic adsorbents the pores or channels have precise