

ULTRA-LIGHT POROUS MATERIALS TAILORED FROM SOLIDIFICATION AND SOLID STATE PROCESSES

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Abstract

A method, conceptually new, for manufacturing hierarchically structured porous materials is presented. The porous structure was tailored during solidification stage and/or solid state transformations. These new materials are called AEROEUTECTICS® and AEROEUTECTOIDS®. Those names refer to a new family of light materials obtained by the substitution with air of selected solid phases (one or more) from a eutectic or eutectoid. This was done with specific treatment of chemical dissolution taking care of preserving the chemical composition and structural integrity of the remaining phases. Some potential uses of these materials are catalysts, adsorbent, super capacitors and solar collectors.

Key words: *light porous materials, eutectic solidification, eutectoids, graphite, cementite, cast iron*

1. INTRODUCTION

What do we mean with the phrase "hierarchically structured materials"? We refer to a set of parts (atoms, molecules, phases) integrated in such a way that an organization of successively subordinate levels can be recognized (hierarchy). The order of succession is determined by a criterion of importance that weighted the relevance of each simple partial action performed by an individual level. The target behind this organization is that finally a more complex functionality can be harmoniously conducted by the whole.

Materials with hierarchical porosity have been heavily involved in newly developed energy storage and conversion systems, and in many others fields, where the demand of higher performance and functionalities grows constantly [1]. As examples of those demands we can mention: provide larger surface areas for reactions, best dispersion of active sites at different length scales of pores, optimization of interfacial transport, and/or shorten diffusion paths or, incorporation of macro porosity to enhance flows, draining or the light harvesting efficiency in devices used for photocatalysis and photovoltaic processes, and so on...

The design of materials having a hierarchical porous structure wherein the pores take different shapes and aspect ratios (cylindrical, flat or irregular channels, slits, etc.) with sizes ranging from nm to mm can be a really challenging and extremely time consuming task (and the manufacturing even worse and costly).

In this work we want to show how we have put to work two very familiar phase transformations, eutectic and eutectoid ones, to achieve this goal. These methods are conceptually new and may be used in a widely variety of metallic, ceramics and organics materials. The only limitation (or advantage depending on the point of view adopted) is that the obtained materials will be always 100% crystalline. An example of the advantages of higher crystallinity could be that it helps reduce the recombination of electron-hole pairs occurring on defects, traps, of the crystalline network. This is a key factor for controlling photo catalysis efficiency.

A eutectic material is produced when a melted solution goes through the following transformation during solidification: L (melted multicomponent solution) → solid α + solid β + ..., at a temperature

that is lower than the fusion temperature of the components of the system, called T_e . At least two solids precipitate simultaneously intimately related but, may be possible that three or more phases solidify. Each eutectic grain consists of two or more interpenetrating mono crystallites that grow coupled through short lengths diffusion controlled mechanism. At the solidification front the atoms of the eutectic partners must move in a direction normal to the global growth direction (GD) so, the speed of the solidification, the growing rate (GR), will determine the spacing between α and β . (See schematic in fig 1).

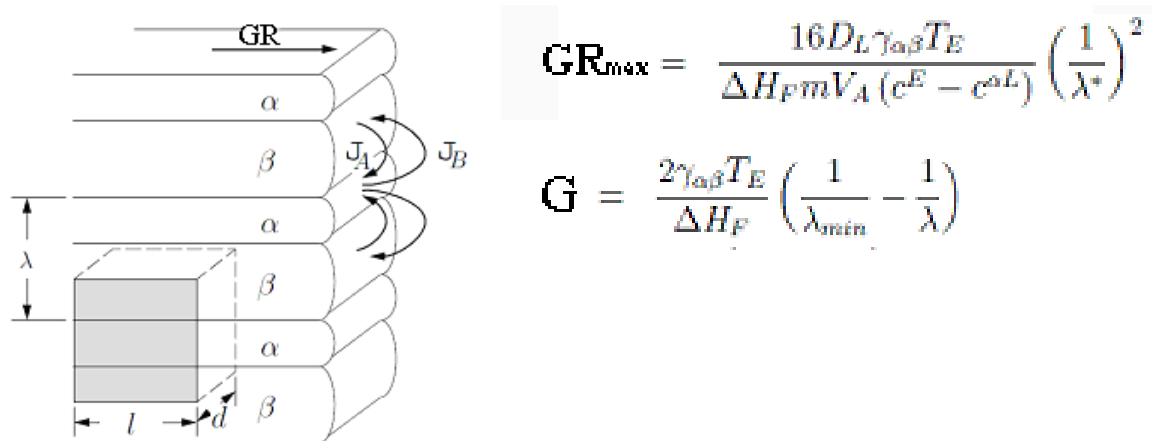


Figure 1: Schematic of lamellar normal eutectic growth mechanism, showing relationship between growth rate vs. spacing and gradient vs. spacing.

The resulting very fine microstructures whose characteristic sizes were controllable by the solidification parameters (GR and the thermal gradient: $G = T_{\infty melt} - T_e$) imposed to the growing biphasic front, reveal the existence of a large clean solid/solid interfaces having well-defined relationships of coupling planes and crystalline directions [2, 3]

Eutectoid materials are the consequence of the following solid state transformation: S (solid multicomponent solution) $\rightarrow$ solid A + solid B. As the diffusion coefficients in solids are smaller ($\sim 10^5$ times lesser than in liquids) it is expected that the resulting microstructures will be very much finer than eutectics ones. Their characteristic spacing will be smaller in orders of magnitude.

These two transformations occur extensively in many systems, (binary or multicomponent). The microstructure will be determined of course by the nature of components and its initial composition and furthermore, by the set of conditions selected to carry out the transformation. There exists an extensive knowledge developed from Physical Metallurgy Principles and Computational Science, especially those referred with solidification and solid state transformations.[4,5,6]) which allow to design and tailoring voluntarily these microstructures.

Taking into account the above we propose that **it is possible to design and fabricate "hierarchically structured materials" using the knowledge and tools available for the control of the microstructure of a eutectic or eutectoid.** Will be enough selecting an appropriate system and the process to design a phase that fits the requirements in terms of chemical composition, crystallography and spatial structure. Once this is done the rest would be the isolation of the selected phase from its partners, taking care to preserve his integrity. That is, proceed **to replace by air the phases accompanying the selected one in the eutectic/eutectoid. We named the new type of porous materials obtained by this way AEROEUTECTICS® and AEROEUTECTOIDS®.**

The big challenge in each case is to find "the" method to dissolve without breaking. But with some experience and practice in chemistry, coupled with patience and expertise, usually a solution can be found and then you have a patentable method.

In this work we will show some results of a method that's working on the ternary system Fe-C-Si (base of gray cast iron). Four aeroeutectic-graphite were extracted from flake cast iron type A, B, D and E (morphologies according to ASTM A247 standard [1]), and a mixed structure extracted from flake pearlitic cast iron consisting of aeroeutectic-graphite plus aeroeutectoid-cementite (Fe_3C). For the aeroeutectic-graphite the replacement by air was performed dissolving all the phases accompanying the graphite; viz: ferrite, cementite, steadite, and a variety of typical inclusions. In the second case, aeroeutectoid-cementite the replacement was achieved dissolving selectively only the ferrite phase. In both cases, patent pending methods were used.

2. EXPERIMENTAL PROCEDURE

2.1 The method to obtain aeroeutectic-GRAPHITE.

Four samples of unalloyed cast iron having four different morphologies: Types: A, B, D and E (ASTM A247 standard), plus a type D alloyed with 2% Cu having pearlitic-ferritic matrix, were selected to obtain aeroeutectic-graphite using a two steps sequence: first, an acid that simultaneously provides a complexing action on Fe cations, was employed. This stage was followed by the dissolution, using a solution containing hydrofluoric acid, of an amorphous precipitate enriched in silicon formed during the first stage.

2.2 The method to obtain aeroeutectoid-CEMENTITE

Two samples having nearly 100% pearlitic matrix (a steel and flake type A cast iron) and the previous mentioned gray type D flake cast iron alloyed with 2% Cu with mixed pearlitic-ferritic matrix, were selected for prepare Aeroeutectoid-cementite through selective dissolution of ferrite phase. The technique consists in a unique step where dissolution is done with a high concentration non-aqueous solution of nitric acid at low temperature.

2.3 The SEM and EDAX characterization

All the extracted aeroeutectic-graphite and aeroeutectoid-cementite were submitted to SEM exploration. Additionally the aeroeutectic-graphite from laminar D cast iron alloyed with 2% Cu was also explored with EDAX before to accomplish the second stage of extraction.

2.4 The characterization of surface areas and pores

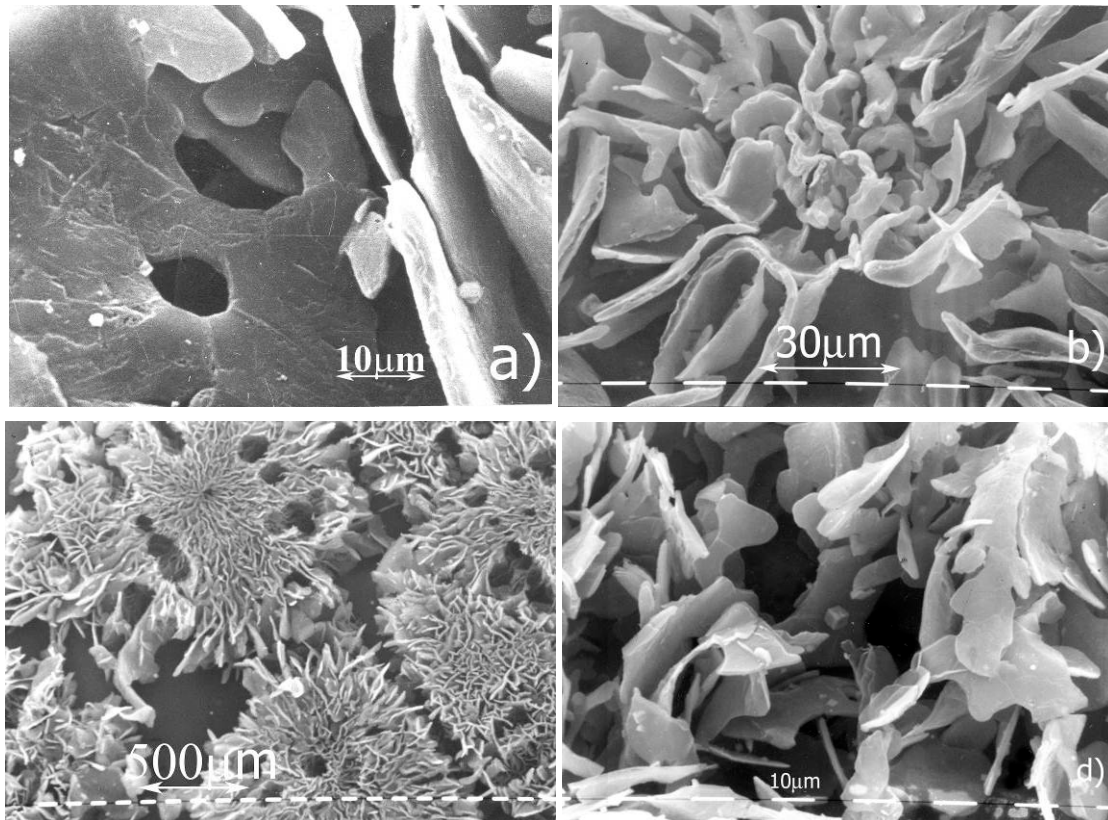
The experiment consists on the determination of the volume of physically adsorbed N_2 by the sample at different pressures, which allowed obtaining the corresponding adsorption isotherm. The textural characteristics were obtained through the analysis of the adsorption isotherm equation by the methods listed and discussed below (see 3.4):

The physical adsorption of N_2 at 77 K was carried out in an automatic volumetric apparatus (Micromeritics ASAP 2010). Before performing the isotherm, the samples were degassed at 100°C for 20 h at high vacuum (10^{-4} Torr).

3. RESULTS AND DISCUSSION

3.1 Aeroeutectic-GRAPHITE

In the following paragraph we will show how the new materials look under Scanning Electronic Microscopy (SEM) exploration.

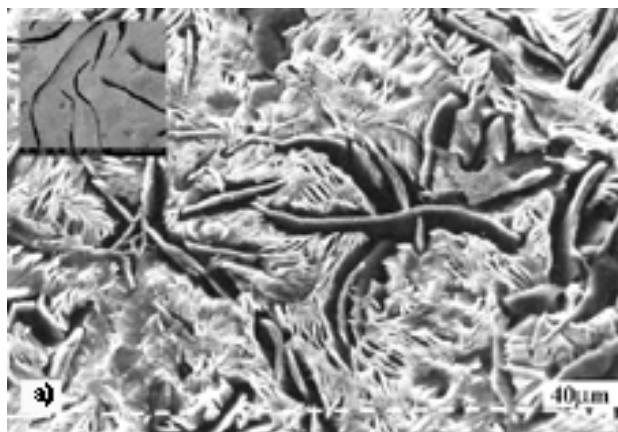


Figures 1 a) to d) show examples of aeroeutectic-GRAPHITE a), b), c) and d) correspond to ASTM types A, B, D and E respectively.

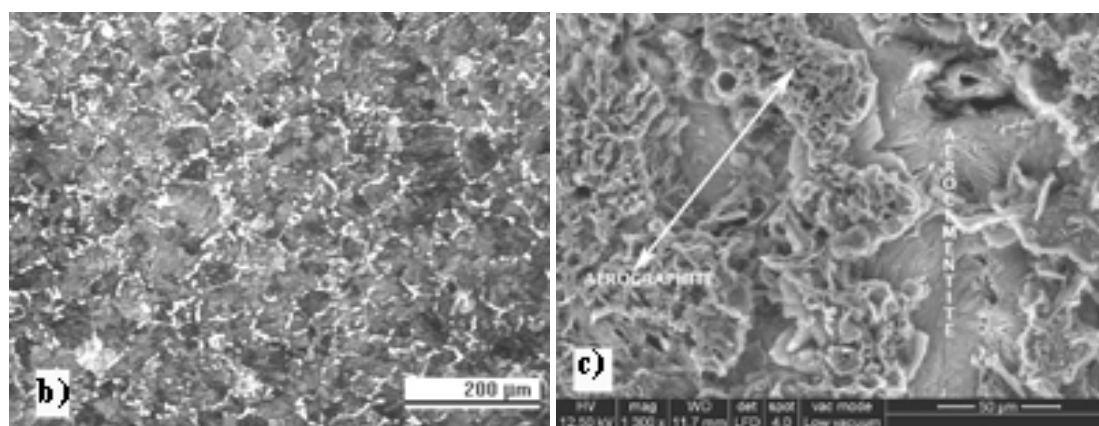
As can be seen with the two steps patent pending process all the phases accompanying graphite in gray cast iron were dissolved. The technique provided an Aeroeutectic-GRAPHITE free of impurities (this is also confirmed by X-Ray diffraction studies, here not reported, that were conducted in another morphologies).

3.2 Aeroeutectoid-CEMENTITE and mixed materials

Figure 2a), b) and c) shows mixed structure formed by Aeroeutectic-GRAPHITE and Aeroeutectoid-CEMENTITE from the Type A and 2%Cu alloyed type D cast iron. In a) composite figure shows, at the upper left corner, an optical micrograph (MO) from flake type A with pure pearlitic matrix and beneath the ferrite depleted sample. In figure 2 b) and c) extracted mixed structure of aeroeutectic-graphite plus aeroeutectoid-cementite from 2%Cu alloyed type D cast iron are shown.



Figures 2 Composed figure: at the left upper corner MO micrograph flake type A with pearlitic matrix, beneath the ferrite depleted sample.



Figures 2 b) and c) extracted mixed structure of aeroeutectic-graphite plus aeroeutectoid-cementite from 2%Cu alloyed type D cast iron at different magnifications

In figure 2 b) low magnification micrograph of mixed sample (aeroeutectic graphite D plus aeroeutectoid cementite) a network of cementite around the eutectics grains can be easily seen. In c) with higher magnification, the big difference between the spacing of eutectic graphite and eutectoid cementite are noticeable.

As was said, in this last sample, Electron Dispersive Energy Analysis of characteristic X-Ray radiation (EDAX) was done. Figure 3 clearly shows a substantial presence of Cu in the mixed structure. It is not a surprising fact because during the first stage of the dissolution (which proceeds with abundant $H_2\uparrow(g)$ evolution) a characteristic coloration of metallic Cu can be observed under naked eye observation all over the surface of the sample. This indicate that, with this technique the Cu in solid solution was removed and then re precipitate again as Cu^0 giving a metallic deposit all over the isolate graphite phase.

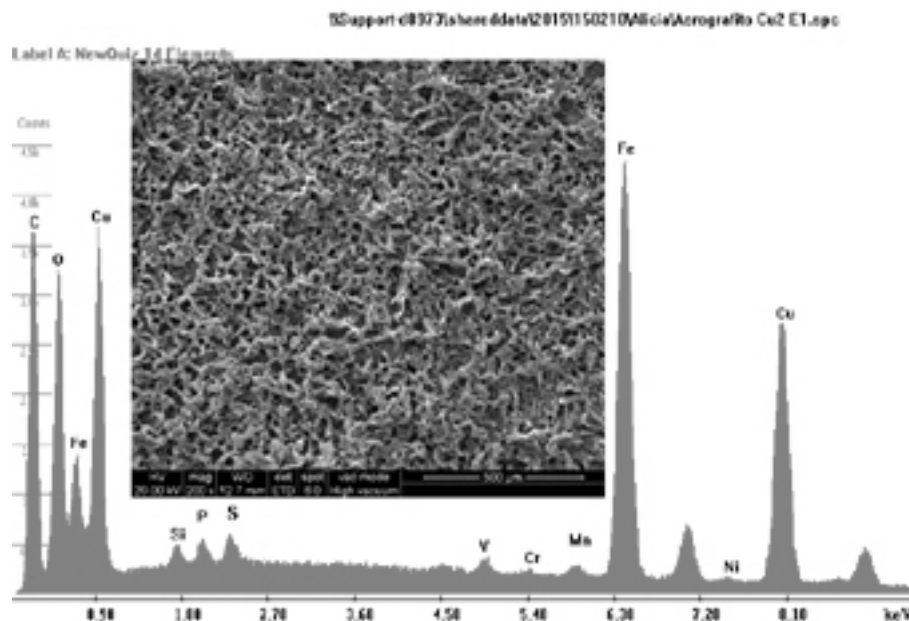


Figure 3. SEM and EDAX of 2%Cu alloyed type D cast iron before second extraction step.

If the same behaviour is reproduced in gray cast iron alloyed with the other members of Cu family, the noble metals Ag and Au, or with noble and semi-noble metals of the adjacent Ni, Pd, Pt family, we would be faced with the possibility of an easy way of fabrication of catalysts, where the active metal would be homogeneously dispersed on a support of mesoporous graphite. The amount of deposited catalytic metal will be directly programmable through the metal concentration dissolved in the eutectic. As concomitantly was also observed a very much lower proportion of amorphous precipitate it seems possible that Cu^0 deposition be in competition with amorphous Si rich phase deposition. Eventually the second stage of the method may be avoidable. This is currently under investigation.

3.3 Surface areas and pores

We show just two examples. Studies were carried on the type E aeroeutectic-graphite. This sample is selected because exhibits the defect known as “spiking”. This is formed by a 3D network of very fine primary dendrites of austenite (See in figure 4a) an scheme at right upper corner) that solidifies when we start from hypoeutectic composition at relative high cooling rates[8]. After the extraction they will becomes an extended and interconnected 3D network of cylindrical channels.

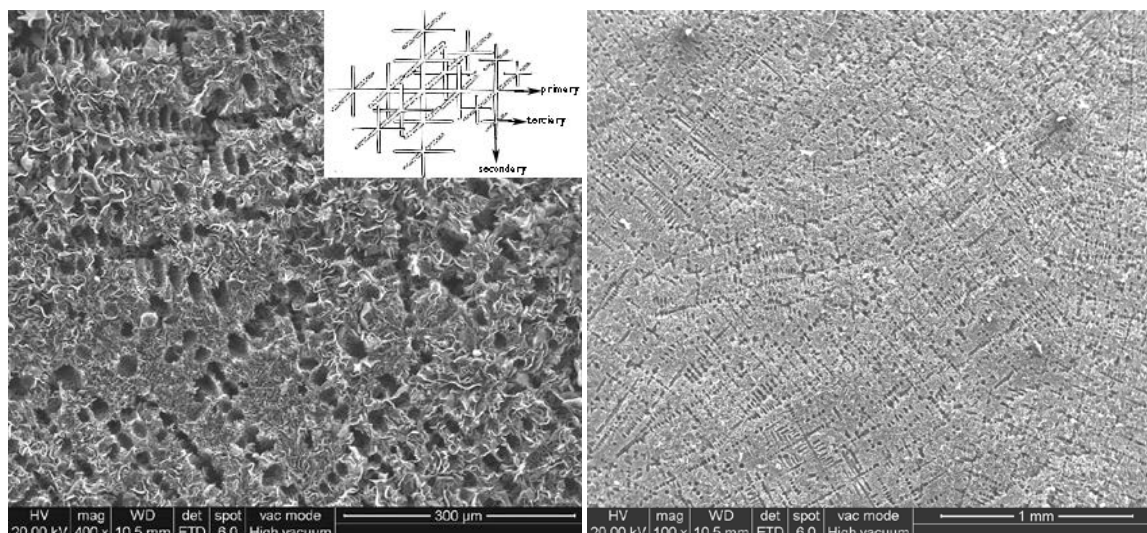


Figure 4 a) Aeroeutectic-graphite type E showing “Spiking” b) low magnification

The second selected sample is the pure aereutectoide-cementite from the 100% pearlitic steel. Here we observed pores that look like slits. They are formed by the stacking of nearly flat walls of Fe_3C separated by extremely thin and regular empty spaces. The pores are nearly 2D channels and are the kind of holes expected to be left behind by removing the ferrite from the lamellar pearlite structure.

To calculate the specific surface area, one of the models most used in mesoporous solids is the one published by Brunauer, Emmett and Teller in 1938 [1]. Because of its simplicity, this model has become the standard measure of comparison between mesoporous solids.

The data of the adsorption isotherm allow knowing not only the area but also the porosity of a solid. Pores are classified into three categories: micropores (pores of 20 Å in diameter), mesopores (pores between 20 and 500 Å in diameter), and macropores (pores of 500 Å or more in diameter).

The Dubinin and Radushkevich model [2], which is based on the Polanyi potential theory, is used for micropores. The Polanyi potential theory considers that there is a potential field in each surface and that the adsorbed layers are contained in a space of adsorption composed of various equipotential contours that define the adsorbed volume.

For mesopores, Barrett, Joyner and Halenda [3] propose calculating the distribution of pores and the average pore size, using a method applied to the desorption branch of isotherms.

The nitrogen adsorption isotherm was carried out in the same conditions used for the determination of the surface area by the Brunauer, Emmett and Teller model. At relative pressures of the isotherm of 10-1, adsorption occurs in multilayers and is used in the Barrett, Joyner and Halenda model to determine the surface area.

In the classification made by Brunauer [4], the isotherm obtained would correspond to type IV, i.e. an essentially mesoporous material. Hysteresis is also observed, which is indicative of the latter. According to the IUPAC nomenclature [5], the type of hysteresis can be classified as H3, characteristic of materials formed by agglomerates of particles in the form of plates, which gives rise to pores in the form of slits. This is largely consistent with that observed by scanning electron microscopy.

Different models can be applied with this purpose according to the range of pore diameter. The model developed by Dubinin and Radushkevich can be applied in the case of micropores to obtain the volume that they occupy (in N_2 at 77 K).

As shown in table 1, in both samples the value of the total pore volume is not so far from that calculated by the Barrett, Joyner and Halenda model for the mesopores. This would indicate that the

structure of the sample is mainly composed of this type of pores. However, in the case of the aeroeutectoid, there is a greater fraction of micropores. This feature, coupled with a lower mean diameter of mesopores according to the Barrett, Joyner and Halenda model, explains the greater specific area of the Barrett, Joyner and Halenda model in the sample corresponding to the aeroeutectoid as compared with the aeroeutectic.

Table 1: Pore characteristics and Surface Areas

Pore characteristics Surface Areas	AEROEUTECTIC from Graphite Type E	AEROEUTECTOIDE from Pearlitic steel
Micropore volume as DR (cm ³ /g)	0.001008	0.034488
Mmesopore volume according BJH (cm ³ /g)	0.103348	0.101672
Average diameter according BJH	229.177 Å	44.485 Å
Area BET	23,4458 m ² /G	189 m ² /G

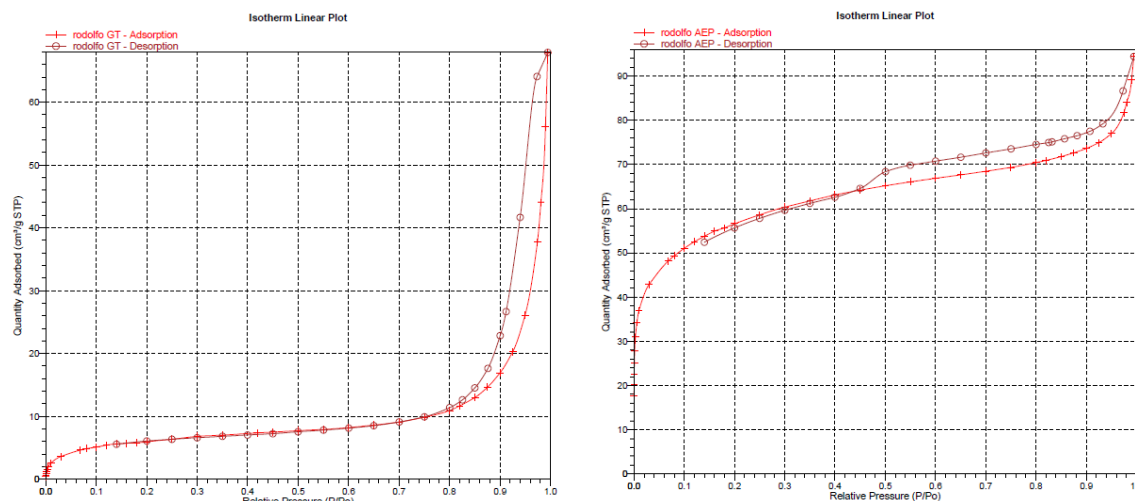


Figure 6: Absorption isotherms a) Aeroeutectic-Graphite left side,-b) Aeroeutectoid Cementite right side

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