WATER ASSISTED THERMAL SEGREGATION
A new way for high purity material preparation

S. Diyani, S. Walter and A. Hadj Mebarek

Ecole Nationale Supérieure de Chimie de Mulhouse, Université de Haute-Alsace
3 Rue Alfred Werner, F-68093 Mulhouse Cedex, France

Abstract

Solid state purification generally requires efficient diffusion mechanisms in order to allow impurity migration towards the sample surface, from which it can be removed by a suitable mean. Since solid state diffusion just becomes efficient near the melting point, generally high working temperatures are required, resulting in expensive, energy consuming processes. The addition of small amounts of a common liquid solvent of both matrix and impurity results, even at low temperatures, in effective diffusion mechanisms the thermodynamical aspects of which are discussed in this work. Thermal cycling enhances the efficiency of the described process. Its concerns industrial and analytical applications.

Keywords: extraction, impurity, KCl, NaCl, thermal segregation

Introduction

High purity material preparation can be managed by numerous ways. However, energy saving remains a permanent trend. Since for crystalline products the diffusion coefficient rapidly increases near the melting point [1], included impurity extraction generally requires near-melting point working conditions in order to allow fast transport mechanisms. Such conditions are generally rather energy consuming and difficult to drive, since the working temperature range is narrow and the thermal homogeneity of the sample difficult to control.

A good alternative to solve this problem is to use a minor quantity of an added solvent, which allows the impurities to migrate towards the grain boundaries by selective dissolution of the matrix near the defects. The grain boundaries consist in matrix saturated solution with an impurity concentration level depending on the thermodynamic activity of the impurity in the matrix.

The potassium chloride-traces of sodium chloride system is taken as an example. At temperatures below 300°C, sodium chloride is not soluble in potassium chloride [2–4]. Under dry conditions, sodium chloride diffusion in the potassium chloride matrix requires temperatures higher than 300°C. This work shows that by addition of less than 1 % water, efficient segregation can be obtained below 60°C, allowing about 50% of the impurity content to be extracted by one purification cycle.

Thermodynamics

Numerous industrial chemicals are produced under far from equilibrium conditions, in order to reach high production rates. However, such working conditions often result in impurity inclusion. The obtained products are generally either polycrystalline aggregates (Fig. 1) or crystalline powders showing more or less defects near the impurity inclusions. The only difference between polycrystalline aggregates and crystalline powders is the absence of bonding grain boundaries in the powdered forms. The described purification process will apply to such products.
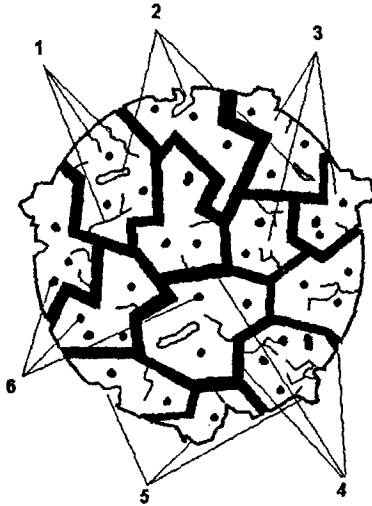

Fig. 1 Polycrystalline aggregate: 1) cracks; 2) vacancies; 3) monocrystalline grains; 4) liquid grain boundaries: saturated solution; 5) surface defects; 6) included impurities

The fundamental reason leading to the behaviour we are going to describe is that atoms (or molecules) present in a surface position have higher energies than the same ones present in bulk positions. Crystallization, or more generally, solidification could not occur if these conditions were not achieved: higher bulk than surface energies would lead to enhance the surface to volume ratio, by phenomena such as embrittlement, crack formations, dissolution, melting or even evaporation depending on the environment.

When crystallization takes place under equilibrium conditions the chemical potentials of the crystallizing species are the same both in the solid and the fluid (melt, solution or gas) phase.

That is: $\mu_S = \mu_f$; where μ_S: chemical potential of the solid phase constituent, μ_f: chemical potential of the fluid phase constituent.

In fact μ_S is a somewhat ambiguous term: the chemical potential of a species is defined by the ratio of energy to the quantity of matter. Only under equilibrium conditions, the surface energies of the bulk and surface constituents are the same. But equilibrium conditions are of poor interest, since nothing occurs when they are

strictly respected. Thus, we will have now to consider how the position of the atoms of the solid phase may alter their chemical potential. As shown before, when crystallization occurs, the atoms at the fluid-solid interface show higher energies than the same ones in bulk positions: $\mu_i > \mu_b$

μ_i: interfacial (or surface) chemical potential, μ_b: bulk chemical potential.

So that one can define a strictly positive term: $\Delta\mu_i = \mu_i - \mu_b$ which is the difference of chemical potential between interfacial and bulk atoms. Figure 1 shows some current kinds of defects present in industrially produced crystalline products: cracks (1), cavities (2), inclusions (6). Cracks and cavities lead to surface creation, inclusions create local strains. When the included impurities are not thermodynamically soluble in the bulk, that means that the strains they create lead to a local high chemical potential μ_d which can be treated the same way as μ_i, and a differential term $\Delta\mu_d = \mu_d - \mu_b$ can be defined. The general expression for the chemical potential of a given atom or molecule in the solid phase becomes: $\mu = \mu_b + \Delta\mu_i + \Delta\mu_d$. For atoms in bulk positions, far from any crystal defect, $\mu = \mu_b$ since for them $\Delta\mu_i = \Delta\mu_d = 0$.

To this point, we just considered the chemical potential of individual atoms. The question now is: what about the chemical potential of atoms in the neighbourhood of surface atoms or crystal defects? To answer this question, one has to consider their mean chemical potential: Figure 2 shows a spherical zone 6 where just the bulk contributes to the chemical potential the value of which is thus μ_b in that zone. Similarly, surface atoms of the zone 8 (Fig. 2) have a typical interfacial chemical potential: $\mu_b + \Delta\mu_i$. The same way, the chemical potential becomes $\mu_b + \Delta\mu_d$ for atoms in contact with the defect generating impurity 11. Thus, for a normal crystal atom density $D = n/V$ (n being the number of atoms crystallizing in a volume V), the average chemical potential μ_{av} of a spherical volume (radius: R) containing x interfacial atoms and y defects is: ($n*$ being the effective total number of atoms)

$$\mu_{av} = (1/n)(n*\mu_b + x\Delta\mu_i + y\Delta\mu_d)$$

$$\mu_{av} = [n*\mu_b] + x\Delta\mu_i + y\Delta\mu_d / [D(4/3\pi R^3)]$$

where in the bulk: $n = n* = D(4/3\pi R^3)$.

For zones with vacancies: $n > n*$, $(n-n*)$ being the number of vacant sites of the volume V. For increasing R, the limit of this function is μ_b. Since μ_b, $\Delta\mu_i$, $\Delta\mu_d$ are all positive terms, that means that the smaller the size of a crystallite, the higher its solubility (or the lower its melting point). The same way, zones like zone 10 (Fig. 2) showing high convexities are more soluble than zones showing lower surface to volume ratii. To the opposite, concave zones (9, Fig. 2) with vacant sites, since $n* < n$, show lower chemical potentials than bulk sites, and are therefore less soluble than bulk constituents. Consequently, under so-called equilibrium conditions, unless it is spherical and defectless, a given crystallite will show differential solubilities depending on its local shape. This will result in dissolving its most convex parts (10, Fig. 2), its kink positions (1, Fig. 2), and in filling up its vacant sites (9, Fig. 2) as shown by Fig. 3, step 1 to 2. Moreover, wide plane surfaces (8,
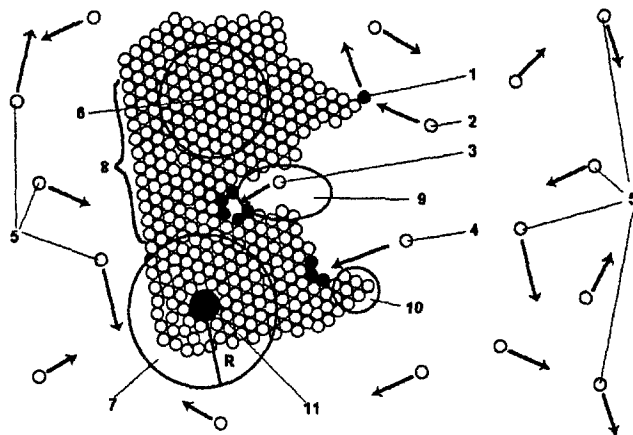
Fig. 2 Behaviour of a monocrystalline grain in a melt or in a solution under close to equilib-
rium conditions: 1) atom in a kink position; 2) atom moving toward a convex (kink)
site; 3) atom moving towards a vacancy; 4) atom moving towards a concave site;
5) free atoms; 6) bulk zone; 7) impurity containing zone; 8) surface zone; 9) concave
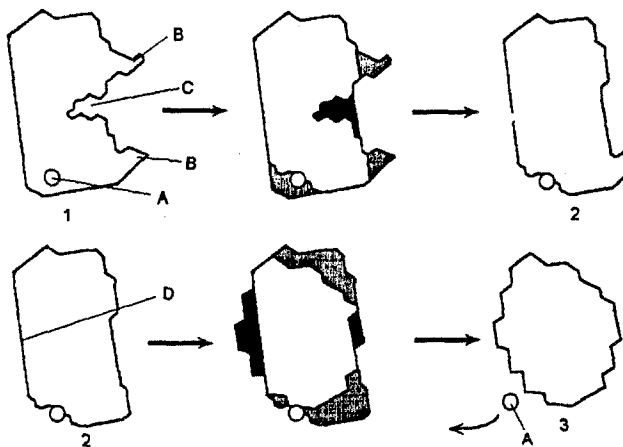zone; 10) convex zone; 11) impurity

Fig. 3 Shape modifications of a crystallite under close to equilibrium conditions: 1) initial
shape; 2) intermediate shape; 3) final shape; A) included impurity; B) convex zone;
C) concave zone; D) flat area

Fig. 2) will reduce their local surface to volume ratio by growing stepwise, as show
by Fig. 3, step 2 to 3. This figure shows also how impurities can become free in the
fluid phase in the same time the crystallite reduces both its internal and surface de-
fects. Heat is the way the required activation energies are brought to the crystals in
order to allow the mentioned transformations to take place.

Experimental

The described results have been observed for several raw KCl salt samples from french mining industries.Their NaCl content is about 1% by weight.The purification process requires following steps: 1) wetting, 2) heating, 3) effective impurity extraction by washing with water or pure KCl solutions.

The water contents of the sample have been determined coulometrically following Bizot's method, the purification efficiency by measuring the potassium and sodium content of both salt and washing solution. The alkali metal determinations have been carried out by atomic absorption spectrometry with a VARIAN AA-6 spectrophotometer. All determinations are repeated three times before and after each step.

Wetting

The raw samples contain about 0.1% (by weight) water unless otherwise specified. For higher water contents, the required amount water is added to the salt in a hermetically closed container kept at 25°C. When the homogeneity control of the sample gives rise to less than 3% standard deviation following Bizot's method, equilibrium conditions are assumed to be reached. Due to capillary effects, the grain boundaries of salt aggregates fill up with a saturated KCl solution containing more or less NaCl depending on the local contamination. (step 1, Fig. 4). The aggregate diameters range from 200 to 800 μm.
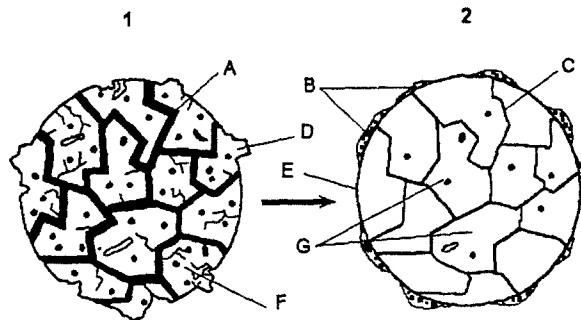

Fig. 4 Effects of heating on a polycrystalline aggregate: 1) wet aggregate; 2) heated and nearly dried aggregate; A) liquid grain boundary; B) fine crystalline impurity layer; C) residual liquid grain boundary; D) surface defect; E) defectless surface; F) contaminated grain; G) purified grain

Heating

Heating is carried out in a weakly ventilated oven (volume 200 dm^3, natural convection through a 10 cm^2 opening at the top) under a partial pressure of water of 10±2 mm Hg. While heating, the mechanisms mentioned above allow the internal grain defects (F, Fig. 4) to migrate towards the grain boundaries A, the sodium chloride concentration of which slowly increases. The slow evaporation of the sol-
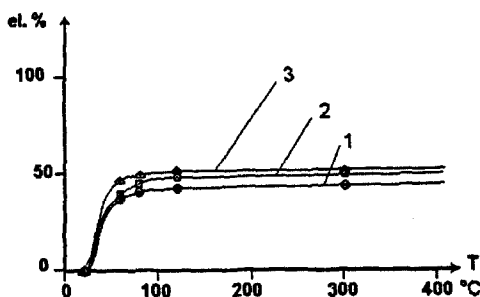
Fig. 5 Eliminated percent impurity *vs.* temperature: 1) after 30 days; 2) after 3 days; 3) after 1 day

vent at the edges of the grain boundaries leads the to very fine (C, Fig. 4) grain boundaries (step 2, Fig. 4), while fine impurity containing crystals (B, Fig. 4) are formed at the aggregate surface. This latter becomes very smooth and sphere-like (E). However, some impurities and defects (G, Fig. 4) remain in the structure and require further wetting-heating cycles to reach the surface. About 40 to 50 % impurity can be removed by one cycle, regardless to the initial impurity content. At the end of the drying phase, the residual water content retained in the grain boundaries by capillary effects is in the range 0.03–0.1% (by weight). Figure 5 shows the eliminated percent impurity content *vs.* temperature for respectively 1, 3 and 30 days stays in the oven at constant temperature. It shows that the purification efficiency is weakly dependent on heating duration, the limit enhancement after a 30 days heating being not better than 20% of the value measured after just one day. To the opposite, in the low temperature range, the dependence on temperature is drastic in the range 20–60°C. This observation must be correlated with the increase of the vapor pressure of water, allowing the intergranular liquid layer to be evaporated at the sample surface, where the dissolved impurities are deposited. Since most of the water is evaporated below 100°C, higher temperatures do not result in efficiency enhancement. This can be brought in correlation with Fig. 6 showing that the higher the initial water content of the sample, the better the consecutive purifi-
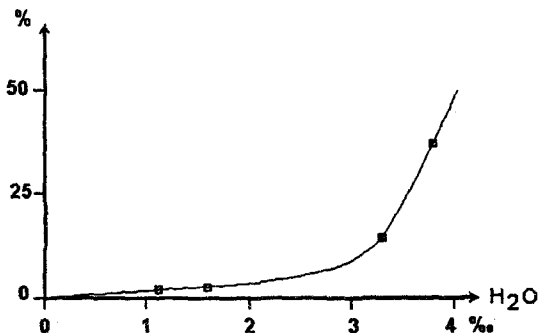

Fig. 6 Percent eliminated impurity after washing *vs.* water content before heating

cation efficiency. Below 0.1% initial water content, no noticeable evaporation occurs during the heating step, the water being retained in the grain boundaries by capillary effects: thus, the transport phenomena being blocked, no purification takes place after washing out.

Washing out

Washing is carried out with aqueous solutions of pure KCl. The KCl concentration can be chosen from zero to saturation. After washing, the obtained effluent is a nearly saturated KCl solution. The KCl concentration of the washing solution has no significant effect on the sodium chloride extraction. The only observable change is the amount of dissolved KCl, which affects the yield of the purification step. Washing out is the step which reveals the impurity migration towards the external surface of the samples by kinetic selective dissolution of the impurity enriched surface layers formed after drying (B, Fig. 4). Figure 7 shows the residual impurity content as a function of the rinsing water amount used to wash out the segregated sodium chloride. The lines 1, 2 and 3 correspond to the same washing conditions respectively applied to 50, 100 and 200 g KCl, filtered on a sintered glass filter (PYREX, porosity 3), with a respective salt layer thickness of 0.5, 1 and 2 cm. The points, A, B and C (Fig. 7), on a horizontal line for approximatively proportional amounts of water show that the only critical factor is the water to salt ratio. The use of high quantities of water does not improve the purification beyond a limit: this observation is a major evidence of the assumed segregation mechanism: the shaded area corresponds to the surface deposited, washable salt, the clear area below corresponds to included salt, which is eliminated at the same rate as the matrix itself. Thus, one cycle purification with huge washing volumes do not lead to good results: the extraction is limited by the included, not washable salt. To the opposite, repeated washing after complete thermal cycling with high wetting (Fig. 6) before heating leads to very efficient purification, correlated with high surface segregation of impurities by edge evaporation of the intergranular liquid, allowing more than 90% impurity to be eliminated after 4 cycles.
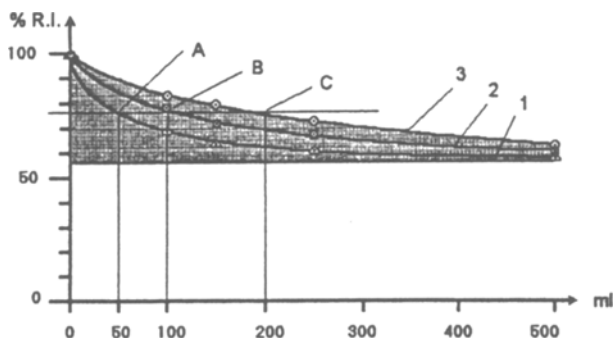

Fig. 7 Effects of rinsing water amount on percent remaining impurity *vs.*: 1) 0.5 cm salt layer (50 g KCl); 2) 1cm salt layer (100 g KCl); 3) 2 cm salt layer (200 g KCl)

Conclusion

This work shows a very inexpensive process able to produce high quantities of medium grade salts. Sun energy heated storage areas can be used to segregate the impurities before washing them out. The results observed for water have a very general thermodynamic support. Thus, they can be easily transposed to other systems, provided one knows the dissolving properties and the vapor pressures of the solvent. On the other hand, diagrams such as Fig. 7 can be useful for analytical purposes, in order to discriminate intragranular from intergranular contamination, when vacuum processes needed for microprobe or electron microscopy observations modify the impurity distribution in the sample.

References

1 W. J. Beek and K. M. K. Muttzall, Transport Phenomena, John Wiley and Sons Ltd, London 1975, p. 226-242.
2 F. A. Matsen and J. Y. Beach, J. Am. Chem. Soc., 63 (1941) 3470.
3 W. T. Barrett and W. E. Wallace, J. Am. Chem. Soc., 76 (1954) 366.
4 B. C. Nguyen, Bull. Soc. Franç. Minér. Crist., (1966) 229.