# Polymer Encapsulation of Arsenic-Containing Waste

M. CARTER,[1] N. BAKER,[2] and R. P. BURFORD[2,*]

[1]ANSTO, New Illawarra Road, Lucas Heights, NSW, 2234, Australia; [2]School of Chemical Engineering & Industrial Chemistry, University of New South Wales, NSW, 2052, Australia

## SYNOPSIS

The potential for encapsulation of arsenic waste by combination with two commodity polymers was evaluated. Initial studies employed nontoxic substitutes, these being gypsum and calcium carbonate, with host polymers being predominately a recycled grade of polyethylene (PE) and a synthetic elastomer. The latter was used at low processing temperatures with rather volatile arsenic compounds. The gypsum caused processing difficulties due to evolved water, but the $CaCO_3$ was able to be readily combined at high volumes. Arsenic trioxide was able to be incorporated at modest levels in PE and was less successfully combined with the rubber. However, the higher processing temperatures needed for PE caused the $As_2O_3$ to sublime. Less volatile calcium arsenite, readily prepared from $As_2O_3$, was able to be mixed at high volume ratios with the rubber, although processing with PE was less successful. These results may be used in conjunction with other methods for stabilization and would be applicable to other forms of medium- to high-level waste. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Previous stabilization studies of $As_2O_3$ using cementatious material[1] showed the waste form passed the toxic characterization leach procedure (TCLP) test,[2] but such material was susceptible to $CO_2$ attack. The hydration product (Portlandite) chemically stabilizes the $As_2O_3$ by forming calcium arsenite. When exposed to carbonated water, this product is broken down to form calcite and $As_2O_3$. The latter is quite soluble (20 g/L) in water and readily leaches out. An avenue to retard the effect of $CO_2$ is to introduce a hydrophobic barrier, such as that provided by polyolefins and related materials. The combination of certain polymers with cement has been the subject of other studies,[3,4] where, generally, the emphasis is on improving toughness or modifying other structural, thermal, or density properties. There has been some interest (particularly in the patent literature) in using impregnation of cement with epoxies and related thermosets to contain low-level radioactive waste,[5,6] but in the present case, such a route would prove prohibitively expensive.

Thermoplastics were then considered as an economic means of providing the necessary incremental enhancement in leaching performance with cement, but here are evaluated in *their own right*, due to the fact that a substantial body of knowledge already exists in inorganic-filled compounds[7,8] and the fact that such materials are readily processed.

The behavior of both polyethylene (PE) and synthetic elastomers such as styrene butadiene rubber in the presence of additives can be broadly summarized as follows: PE can be combined with high levels of fillers which range from nonreinforcing, cheapening additives such as clay, to specialty compounds such as microspheres (to reduce SG), flame retardants, and electrical conductors. Generally, hardness is increased, but toughness and ductility suffer, so that inherently ductile ($\varepsilon_b > 500\%$) polymers will become brittle ($\varepsilon_b \ll 100\%$) at filler loadings greater than about 50 vol %. In many cases, such embrittlement is not crucial, and the advantages outweigh the alteration in mechanical performance. In the present case, any encapsulated waste would either be further combined with cement or buried, and thus physical properties are not important.

In the case of elastomers, the mechanism of filler–polymer interaction is quite different, and, generally,
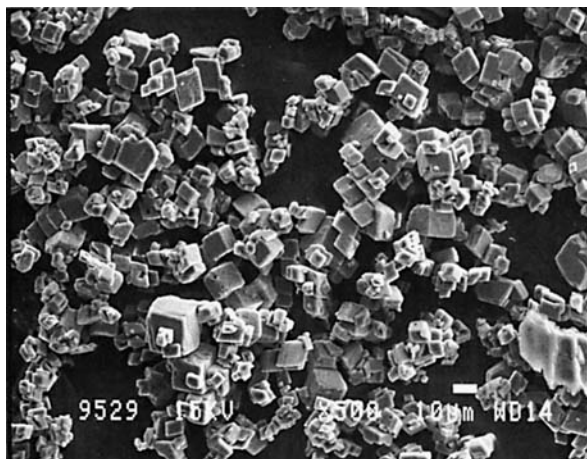
**Figure 1**   SEM micrograph of calcium carbonate powder.

elastomers are routinely combined with high levels of inorganic additives. In some cases, the primary role of filler is as an extender (e.g., clay and calcium carbonate), but retention of useful properties is still possible even when volume loadings exceed 70%.[9] For reinforcing fillers such as carbon black and silica, enormous and necessary improvements in physical properties (breaking stress and strain, toughness, and abrasion resistance) are commonly achieved.[10]

There have been a diversity of methods used for polymer encapsulation of low-level radioactive waste using thermosets and related crosslinkable systems (e.g., Refs. [11-15]), but the literature relating to thermoplastics is more restricted. Moriyama et al. at the Japan Atomic Energy Res. Lab, Tokai, solidified dried filter sludge with PE[16,17] and the Brookhaven group (Franz and Colombo[18-21]) evaluated several polymers (but mainly PE) with low-level waste including incinerator ash, salt wastes, and ion-exchange resins.

From the Brookhaven papers, leaching tests of the resulting waste leads to the conclusion that encapsulation of dry powdered wastes in polyethylene is feasible, with the modified polymer demonstrating good leaching characteristics and high compressive yield strength, but the study did not include any evaluation of arsenic-containing waste, nor were any morphological studies undertaken.

In our work, the processing and structural characteristics of filled elastomer and PE is reported. It is recognized that the cost of even commodity polymers is expensive in the context of large volume waste encapsulation. However, the strategy described may be feasible where either extremely high filler volume loadings can be reached, where waste is extremely hazardous and/or concentrated, or

where a cheap (e.g., waste/recycled) form of thermoplastic becomes available.

## EXPERIMENTAL

### Materials

High-density polyethylene (HDPE) as recycled black pellets generated from dairy and juice containers (Grade HD119R, Kemcor) was obtained from OJ Plastics, Regents Park, Sydney, Australia. According to the specification sheet,[22] it is a rigid grade with an MFI of 0.4–0.8 g/10 min (190/2.16) and a density of 0.964–0.970 g/cm$^3$. It has a melting point of 130°C and a recommended processing temperature ranging from 180 to 210°C.

Solprene 1204 (Phillips Australia Chemicals) is a random styrene butadiene copolymer with a 25% styrene content. It is made by an anionic polymerization process to a nominal Mooney viscosity of 56 $ML_{1+4(100°C)}$.

Gypsum was provided as a fine powder by Blue Circle Southern (Berrima) and is > 95% pure. Calcium carbonate was analytical grade (>99%), BDH Chemicals, Australia, and has a mean particle size of 33 $\mu$m as determined by the Malvern Mastersizer method. It has a rhombohedral habit, as shown by the SEM in Figure 1.

High-purity (>99%) arsenic trioxide was donated by CSIRO and has a mean particle size of 50 $\mu$m and an octahedral habit as shown in Figure 2. The calcium carbonate and the $As_2O_3$ are relatively isotropic, and the Malvern data show that both have Gaussian particle-size distributions and similar polydispersity. The gypsum, by comparison, has a prismatic habit.
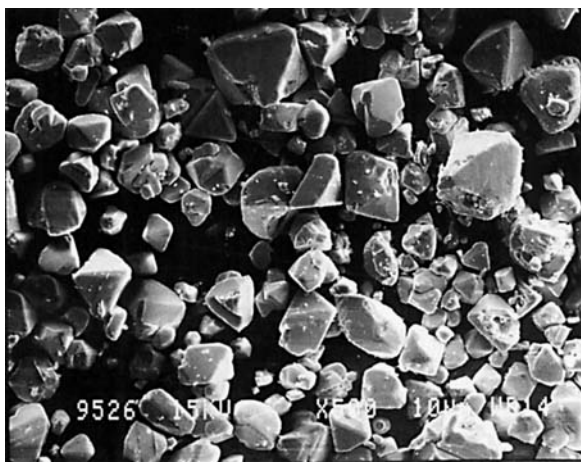


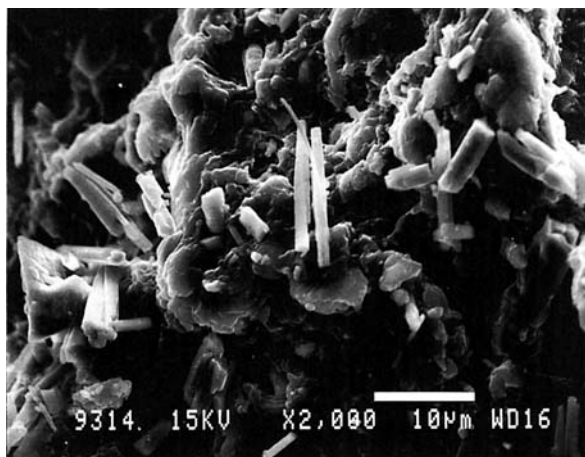**Figure 2**   SEM micrograph of arsenic trioxide powder.

**Figure 3**   SEM micrograph of gypsum in PS (fracture surface).

Calcium arsenite was prepared by mixing $1 M$ calcium oxide (in hydroxide form) with $0.5 M$ $As_2O_3$ with approximately 0.5 L water. The dried residue was then readily transformed to a fine soft powder.

## Processing Techniques

Initial trials were conducted with $CaCO_3$ and gypsum in a BOY 15 S injection-molding machine using barrel temperatures of about 160°C to form tensile and impact bars. Subsequent experiments were performed in a Haake 600 series internal mixer using a 70 cm$^3$ capacity chamber, Banbury rotors, a rotor speed of 60 rpm, and temperatures of 200°C for the HDPE and 100°C for the Solprene 1204. Modifications to the internal mixer technique were introduced to reduce the risk of toxic exposure, when $As_2O_3$ and calcium arsenite were used as fillers.

## Microscopic Methods

Filled polymers were cut and polished using conventional metallurgical methods (e.g., final polish with a 1 μm diamond paste). Strips of Solprene compounds were frozen in liquid nitrogen and then fractured. Fillers, fractured-filled compounds, and polished sections were examined, after carbon coating, in a JEOL JXA 840 SEM, with secondary electron detection generally providing adequate contrast between filler and polymer. In some cases, backscattered detection methods were used for elemental contrast.

## RESULTS AND DISCUSSION

### Injection-Molding Studies

Gypsum was dry mixed with both polystyrene and HDPE and fed to the injection molder using a conventional hopper. Levels of up to 50 and 30 wt % were achievable, respectively, beyond which jamming at the die occurred. Evolved moisture from the gypsum led to trapped water which escaped violently if mold opening occurred before molded parts had cooled. Incomplete dispersion also occurred with large white particles being unevenly distributed in the polymer matrix. The rather short mastication time and nonoptimized molding conditions lead to imperfect specimens; it was considered that adjustments in blending technique were more practically achievable in the internal mixer, particularly at high-volume loadings. Fracture surfaces of gypsum-filled PE and PS are shown in Figures 3 and 4 and show that the fibers do not adhere well into the polymer matrix. The gypsum studies were discontinued, as this filler does not serve as a suitable model compound for calcium arsenite or $As_2O_3$. The gypsum is hydrated and prismatic, whereas the arsenic compounds are not. It was surprising that the gypsum incorporated into the PS at higher levels, although this might be partially attributed to early water loss at the higher temperatures used.

The calcium carbonate was able to be taken up at up to 50 wt % in both PE and PS, beyond which the machine jammed. Inadequate wetting is the probable cause; further processing refinement was plausible but not attempted. A fracture surface of the calcium carbonate in PS is shown in Figure 5 and reveals the $CaCO_3$ as previously shown in Figure
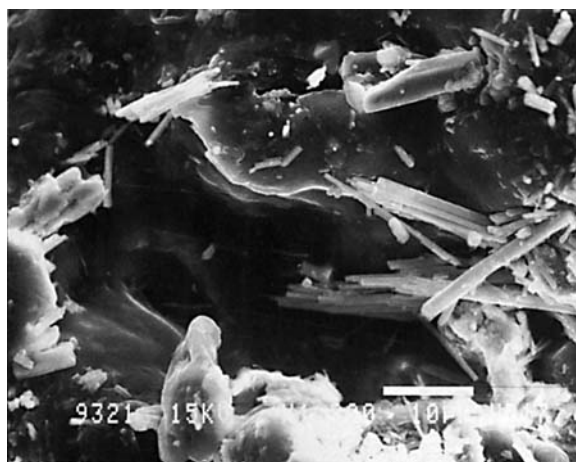


**Figure 4**   SEM micrograph of gypsum in PE (fracture surface).

**Figure 5** SEM micrograph of calcium carbonate in PS (fracture surface).



**Figure 7** SEM micrograph of calcium carbonate 60 vol % in PE (polished surface).

1. The PE remained tough and ductile; a cut section (Fig. 6) has caused masking of the filler during sample preparation. In both cases, visual inspection of the test bars indicates that dispersion is incomplete.

### Internal Mixing Studies

In this phase of the work, two polymers and three fillers were used. It is convenient to divide this section into HDPE and Solprene studies, as the processing temperatures and outcomes were quite distinct.

### High-density Polyethylene

This was first trialed with nontoxic $CaCO_3$ in the Haake mixer at 200°C, and a 60 vol % loading was

easily achieved and we envisage that even higher loadings are possible. A polished surface of the 60 vol % compound is shown in Figure 7, with the lighter domains being calcium carbonate-rich. A few artifacts due to voids in the compound can also be found. A similar procedure was employed with 50 wt (i.e., 20 vol) % $As_2O_3$. It was quickly discovered that the $As_2O_3$ had a dramatic effect, with the viscosity increasing greatly and the plastic becoming unworkable.

A section of the filled compound is shown in Figure 8 (fine cracking is due to some separation of the carbon coating caused by polishing oil residues). The reason for the viscosity increase is not known, but may be due to chemical reaction. However, it is quite evident that the $As_2O_3$ has sublimed and recrystallized in a different form to that previously shown in
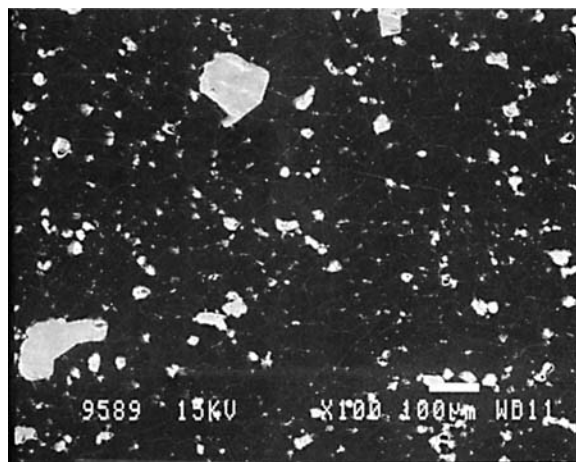


**Figure 6** SEM micrograph of calcium carbonate in PE (fracture surface).



**Figure 8** SEM micrograph of arsenic trioxide 50 wt % in PE (polished surface).

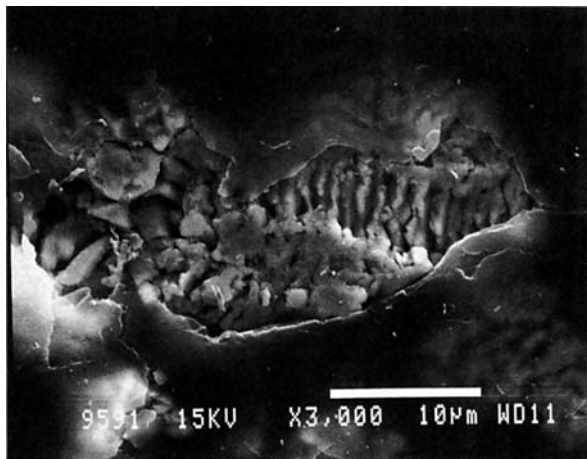**Figure 9**   SEM micrograph of arsenic trioxide in PE (polished surface).



**Figure 10**   SEM micrograph of calcium arsenite PE (surface).

Figure 2. The dendritic, encapsulated $As_2O_3$, is shown in Figure 9. We are now aware that $As_2O_3$ sublimes at about 200°C, so that routes in which either a temperature stabilized form of As or a lower processing temperature polymer is employed need to be followed.

The former avenue was pursued by using calcium arsenite, which we showed separately to lose negligible weight at 225°C. This was also mixed in PE, but only 17 wt % was able to be incorporated. The polymeric mass became very sticky, with globules of fused filler appearing at the surface (Fig. 10).

Backscatter images at higher magnification confirmed that the nodules are indeed arsenic-rich, as seen in Figures 11 and 12, respectively. Some minor physical breakdown of the calcium arsenite particles occurs, as seen by the fine particulate matter away from clusters in Figure 12.

## Styrene–Butadiene Rubber (Solprene 1204)

Trials using calcium carbonate revealed that up to 50 vol % filler could be readily incorporated. However, at higher loadings, viscosity increased abruptly and the shear pins of the Haake mixer ruptured. Improvements could be made using double-style mixers and/or addition techniques which overcome the low bulk density of this filler. The filler is somewhat hard to resolve by SEM as particles are very fine, but Figure 13 indicates that dispersion is of a high order.

The second trial was with arsenic trioxide, and here we failed to achieve our ambitious target of 50 vol % (i.e., ≈ 80 wt %). We estimate that 40 vol % can be incorporated, but beyond this level, the rubber becomes unworkable. Although the viscosity did not
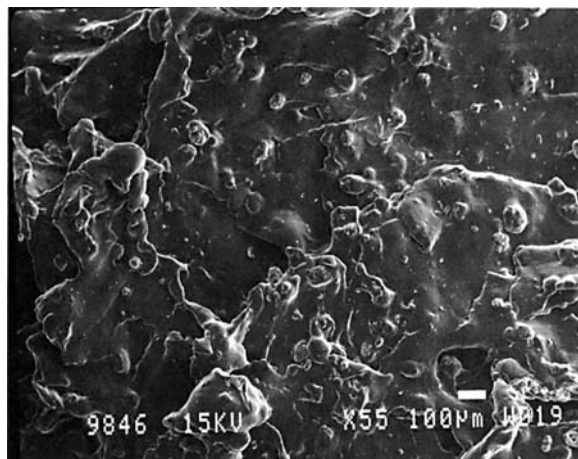
appear to increase dramatically, the compound was tacky and hard to process. The fracture surface shown in Figure 14 reveals that (unlike for PE), the morphology of the filler is retained (compare with Fig. 2). The contrast in behavior with the two different polymer matrices is undoubtedly a reflection of the two processing temperatures and also the associated difference in rheological behavior. At higher magnification, it can be seen that the arsenic trioxide is intimately encapsulated within the matrix, with no voiding between filler and rubber.

Compounds containing 25, 40, and 50 wt % calcium arsenite were also prepared in the internal mixer and these are shown as liquid nitrogen-fractured surfaces in Figures 15–17. At the lower loading, the tear morphology of the rubber itself can be seen, and the hollow sphere structure of the filler can be
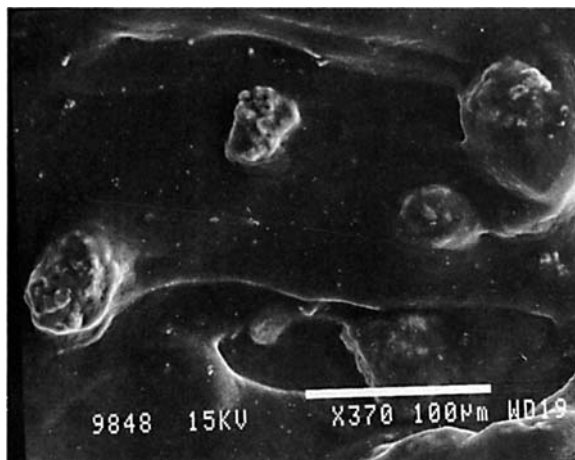


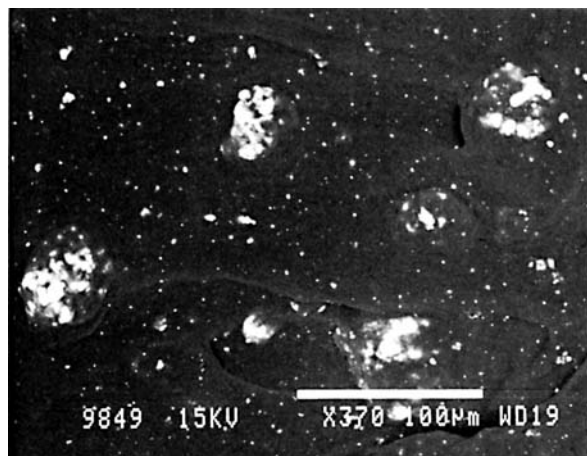**Figure 11**   SEM micrograph of calcium arsenite in PE (surface).

**Figure 12**  SEM back scattered image of calcium arsenite in PE (surface).



**Figure 13**  SEM micrograph of calcium carbonate in Solprene 1204 (fracture surface).

resolved. This is a consequence of the drying step during preparation and accounts for the low apparent bulk density ($\approx$ 1.7 g/cm$^3$) of this filler. The increasing ratio of filler as we progress from Figure 15 (25%) to Figure 17 (50%) is also obvious. These compounds were able to be processed with no difficulty.

To examine the interface between filler and Solprene, all three compounds were viewed at higher magnification. Figure 18 (25% filler) is typical and shows several features. First, interfacial contact is extremely high, indicating good adhesion. Second, there are large polyhedral macropores, which we attribute to crystal growth on prepared lattice planes. Finally, the solid itself is otherwise reasonably well compacted.
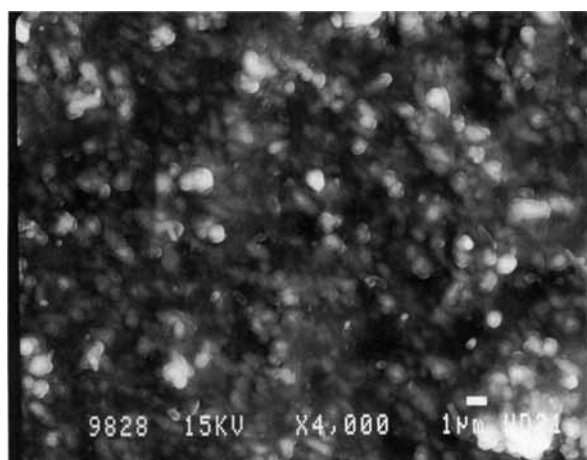
An attempt was made to vulcanize the calcium arsenite-filled Solprene 1204 by adding 2.5 phr "dicup 40R" (i.e., 2.5 g of 40% pure dicumyl peroxide was added to 40 g rubber, together with added filler). We found that this material rapidly foamed to a crumbly, low-density mass, unsuitable for further molding. Thus, we were unable to prepare vulcanized samples for microscopic examination or physical testing. Other strategies using sulfur, etc., might be more appropriate.

## CONCLUSIONS

We conclude that it is possible to incorporate significant loadings of arsenic-containing filler into polymer matrices but that several factors need to be
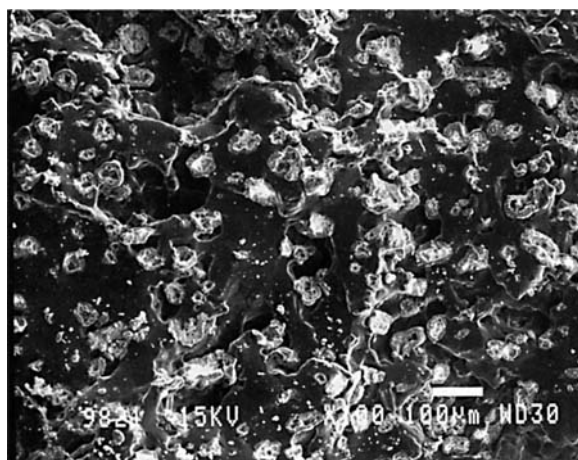


**Figure 14**  SEM micrograph of arsenic trioxide in Solprene 1204 (fracture surface).



**Figure 15**  SEM micrograph of calcium arsenite 25 wt % in Solprene 1204 (fracture surface).

**Figure 16** SEM micrograph of calcium arsenite 40 wt % in Solprene 1204 (fracture surface).



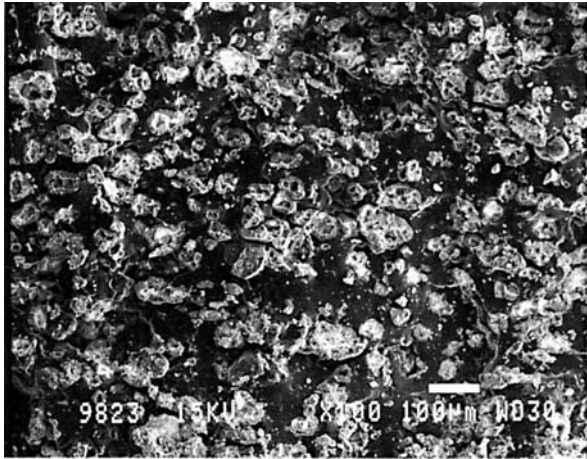**Figure 18** SEM micrograph of calcium arsenite in Solprene 1204 (fracture surface).

acknowledged if large-scale encapsulation is to be efficiently performed. With polythene, it is evident that conventional fillers can be readily accommodated, but these are inert and nonvolatile and so are poor indicators of the behavior of certain arsenic compounds. Volatile concentrates including $As_2O_3$ are not suitably bound into PE, as the processing temperatures generally employed approach the sublimation temperature. This means that compounding is inefficient and hazardous. When $As_2O_3$ is stabilized with calcium oxide, volatility decreased, but loadings remained low.

The use of an elastomer appears to have greater potential, as higher volume loadings are possible. The $As_2O_3$ can be incorporated at reasonably high loadings, but the calcium arsenite compound processes better and a filler loading of up to 50 wt % is
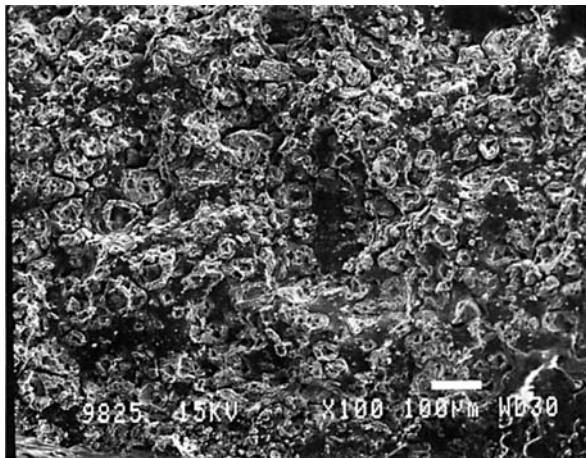
easily reached. We believe that if the calcium arsenite can be prepared with a higher bulk density, very high wt % filled compounds should be possible. Such materials may represent a partial solution to $CO_2$ leaching problems associated with other cementatious fixation systems.

**Figure 17** SEM micrograph of calcium arsenite 50 wt % in Solprene 1204 (fracture surface).

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