

consortiums such as Dow-Corning, Elkem/Exxon, Siemens, NEDO, to mention the most accomplished [45–52]. Quartz or silica sand selected for their original purity were chemically treated by leaching or precipitated from water glass solutions. Purified carbon black was used as the reduction material in most of these approaches. The morphology of sand or precipitated silica and carbon black are quite different from, respectively, lumpy crystalline quartz and bulk carbon, charcoal or woodchips currently used in the carbothermic reduction. New technologies, in particular, to agglomerate the powder-like raw materials had to be developed. Pellets consolidated by means of organic non-contaminating binders (e.g. sucrose) or rice hulls perceived as potential high-volume, low-cost raw materials since they contained both silica and carbon are worth mentioning. Extruded pellets of cocked rice hulls, with sucrose, as a binder appeared to be reactive in the submerged arc furnace technology. Using these special raw materials, boron and phosphorus were found in the range of 1 to 4 ppm(w). In standard metallurgical grade, B and P range between 7 and 50 ppm(w), typical average values being around 25 ppm. The boron level achieved with rice hulls could be as low as 1 ppm(w). However, phosphorus was as high as 40 ppm(w) and would request an additional and specific treatment to make use of this source of silicon in solar cells.

5.7.2.2 *Post-treatment by chemical leaching*

Metallic impurities segregate at the grain boundaries, forming intermetallic phases with silicon, basically made of silicides and silicates. Hydrometallurgical upgrading of silicon by acid treatment and leaching has a long history. The *Silgrain* © process, a trademark of Elkem ASA, is currently producing 30 000 MT metallurgical grade silicon by refining ferrosilicon (90% Si) in an acid liquor of ferric chloride. The process is particularly efficient in removing iron and transition elements because these have very low segregation coefficients in silicon. The dissolution of iron and the transition elements in the leaching liquor is eased and enhanced by the formation of stable intermetallic phases with Al, Ca or isostructural elements, for example, Sr, Ba, Ga or a lanthanide. The process has been further developed during the past 15 to 20 years with solar grade silicon as an objective [53–56].

Surface treatment or leaching by hydrofluoric acid or by HCl/HF mixtures is also well known to wash out residual impurities present as oxides and silicates. Grinding silicon prior to leaching to increase the surface exposure is a way to enhance the purification [57, 58]. Acid leaching has therefore been envisaged by several groups and companies, for example Wacker and Elkem, as a post-treatment purification after the carbothermic reduction [53–58].

However, it must be emphasised that this method cannot in practice refine silicon below the dissolution limit characteristic of each element at the solidification composition. For the major impurities Fe, Ca and Al present in metallurgical grade silicon the limit of dissolution as obtained from classical refining in a ladle exceeds by far the ppm level. Effective post-treatment leaching of metallurgical grade silicon has made it possible to achieve less than 10 ppm(w) for these major elements and less than 1 ppm(w) for minor transition elements. One pass of directional solidification was then envisaged as sufficient to achieve the requested purity for solar cells.