The acid treatment or leaching methods is not effective in removing interstitial and substitution impurities such as boron, carbon and oxygen. Adding Ca to the silicon alloy prior to acid treatment, however, proves that P could be reduced by a factor of 5 down to a concentration less than 5 ppm(w), probably because P is dissolved in calciumsilicide [55, 56]. Adding barium also proves some effect on boron dissolution.

5.7.2.3 Post-treatment by extraction metallurgy in ladle

Post-treatments of liquid silicon are common practices in refining metallurgical grade silicon for applications in aluminium and chemical industry. The objective is then to adjust Al, Ca and possibly C to a suitable concentration of some hundreds or thousands of ppm(w). To that respect the reader may with great benefit consult Schei's *et al.* comprehensive handbook [13, 23]. As described above, crystallisation and leaching are efficient means of removing chemical elements with high ability to segregate from liquid to solid silicon, that is, Fe, and most of the metallic transition elements. Extraction metallurgy from a liquid phase of silicon, either liquid–liquid, liquid–solid or liquid–gas, has received considerable attention in order to remove the critical elements P, B and C. When silicon is kept liquid, it is possible to displace the equilibrium between both phases present and gradually remove the unsuitable impurity, by continuously extracting it.

Impurity(liquid silicon) = Impurity(liquid slag)	*Ksi/ls*
Impurity(liquid silicon) = Impurity(solid slag)	*Ksi/ss*
Impurity(liquid silicon) = Impurity(gas)	*Ksi/g*

Particular attention has been paid to boron and phosphorus because these elements are the major *p*- and *n*-type dopants of silicon and because they coexist in metallurgical grade silicon in concentration of one or two orders of magnitude too high for solar cell applications.

Boron has nearly the same affinity towards oxygen as silicon. Boron forms gaseous suboxides BO being analogous to SiO, and its stable oxide B_2O_3 behaves similar to SiO_2 in the presence of alkaline earths at slag-forming temperatures. Therefore, there are good reasons to expect the removal of boron as an oxide constituent of the extracting slag or as a gaseous suboxide at elevated temperature. Both theoretical possibilities have been experimentally verified.

Since the work published by Theuerer in 1956 [59], it has been known that liquid silicon becomes purified with respect to boron when brought in contact with a gas mixture of $Ar–H_2–H_2O$. The sole role of H_2 and H_2O assisting the extraction has been emphasised by several authors such as Khattak *et al.* [60–63], whereas Amouroux, Morvan *et al.* of the University of Paris [64–67] and the Japanese group of Kawasaki Steel/NEDO [68–72] have underlined the benefit of using an oxidative plasma in the presence of moisture and hydrogen. Amouroux, Morvan *et al.* have also shown that boron elimination was enhanced when fluoride, for instance in form of CaF_2, was injected into the plasma gas.

Experiments in removing B by slag extraction have been done by several companies and groups including Kema Nord, Wacker, Elkem and NEDO/Kawasaki. Schei [73] has