Nanoparticles of zero-valent iron (nZVI) have been recognized as a promising modern nanomaterial well applicable in waste-water treatment and in many other branches of industry and environmental engineering. In order to perform the cheap and reproducible synthesis of nZVI, the heat-induced solid-state reactions under controlled hydrogen atmosphere were employed. For this purpose, hematite $\alpha$-Fe$_2$O$_3$, maghemite $\gamma$-Fe$_2$O$_3$, goethite FeOOH and ferrihydrite 5Fe$_2$O$_3$·9H$_2$O were tested as suitable solid precursors. The process of nZVI synthesis was in-situ monitored by X-ray powder diffractometer (XRD) equipped with a high-temperature reaction chamber operating at temperatures up to 900 °C and at hydrogen gas pressure up to 10 bars. The results of non-isothermal and isothermal heating show that the conversion of various iron oxides into the metallic $\alpha$-Fe (nZVI) take place at various temperatures ranging between 260 °C and 600 °C depending on the precursor and hydrogen gas pressure/flow.

The transformation mechanism involves the initial reduction of the starting iron oxides into either pure nanocrystalline magnetite Fe$_3$O$_4$ (for $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ precursors) or mixture of Fe$_3$O$_4$ and wüstit FeO (for FeOOH precursor) followed by their reduction into $\alpha$-Fe nanoparticles (Figure 1). Only in the case of
amorphous ferrihydrite, the transformation does not involve any intermediate crystalline phase(s) and, thus, the X-ray amorphous material is reduced directly to $\alpha$-Fe. The size of resulting nZVI particles vary from 30 to $\sim$170 nm depending on the conditions of synthesis (Figure 2).

![Fig 2. Two-step evolution of the size of $\alpha$-Fe coherent domains depending on the temperature of synthesis form ferrihydrite (Fh) precursor (calculated from variable-temperature XRD using Rietveld analysis).](image)

In a consequence to successful laboratory-scale synthesis of nZVI, the transfer of targeted technology to a semi-industrial scale was realized. In the last step, we tested various surfactants (Tween80, Acrylate copolymers etc.) in order to ensure long-term protections of nZVI particles against agglomeration and spontaneous oxidation. The results confirm that the developed surface stabilized nanomaterials (Figure 3) possess the required migration properties in the underground water environments with a high efficiency in decomposition of various organic and inorganic pollutants.

![mean ~50 nm (30 to 70 nm)](image)

![Tween 80](image)

**Fig 3.** Left - scanning electron micrograph of nZVI particles prepared from hematite; right - transmission electron micrograph of nZVI particles stabilized using of Tween80.