NanoRem: Nanoremediation for Soil and Groundwater Clean-up - Possibilities and Future Trends

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1 Introduction

NanoRem was a research project, funded through the European Union's Seventh Framework Program for research, technological development and demonstration under grant agreement no. 309517. NanoRem focused on facilitating a practical, safe, economic and exploitable nanotechnology for *in situ* remediation of soil and groundwater. This was undertaken in parallel with developing a comprehensive understanding of the environmental risk-benefit for the use of nanoparticles (NPs), their market demand, overall sustainability, and stakeholder perceptions. The project was designed to unlock the potential of nanoremediation processes from laboratory scale to end user applications and to support both the appropriate use of nanotechnology in restoring land and water resources as well as the development of the knowledge based economy at a world leading level for the benefit of a wide range of users in the EU environmental sector.

The NanoRem consortium was multidisciplinary, cross-sectoral and transnational. It consisted of 29 partners from 13 countries (Fig. 10) organised in 11 work packages. The consortium included 19 of the leading nanoremediation research groups in the EU, 9 industry and service providers (7 SMEs (small and medium sized enterprises)) and one organisation with policy and regulatory interest. The consortium was co-ordinated by the VEGAS team (Research Facility for Subsurface Remediation) from the University of Stuttgart in Germany.

The overall aim of the NanoRem project was to demonstrate that the application of NPs is a practical and reliable method for the treatment of contaminated soil and groundwater. NanoRem provided a direct link between SMEs on the production side and SMEs on the application side of groundwater remediation using NPs.

2 What does Nanoremediation mean?

Nanoremediation means the use of nanoparticles (NPs) for treatment (remediation) of contaminated soil and groundwater. Depending on the use of different particles types nanoremediation processes generally involve reduction, oxidation, sorption or a combination of these. NPs are usually defined as particles with one or more dimensions <100nm, but they can include larger composite particles with embedded nanoparticles. The main focus is on source treatment in the saturated zone, but plume treatment is also an option (Fig. 1). It is applicable below buildings, "independent" of application depth. Different NPs can be used for various contaminants. But it is still an innovative technology.

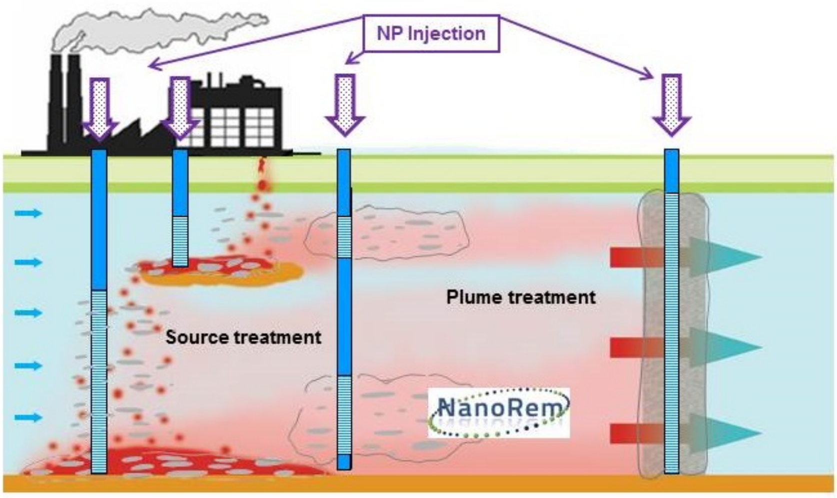

Figure 1: Possibilities for Nanoremediation

3 Project Structure

The project structure is depicted in Figure 2.

The *Design and Production Group* was comprised of two work packages (WP2 & WP3) to facilitate the focus on different NPs and their corresponding production and application strengths.

The Performance Group was established to bridge the gap from production to application (WP4-WP7), to work closely together to ascertain potentials and limitations of NPs, and to extend the limits of economic and ecological NP application.

The *Application and Dissemination Group* was responsible for successfully transferring the technology to the end-user. This comprised the proof of concept in large scale indoor experiments (WP8), the demonstration at a number of pilot sites (i.e. field tests, WP10), risk assessment and sustainability and lifecycle assessment considerations (WP8 & WP9).

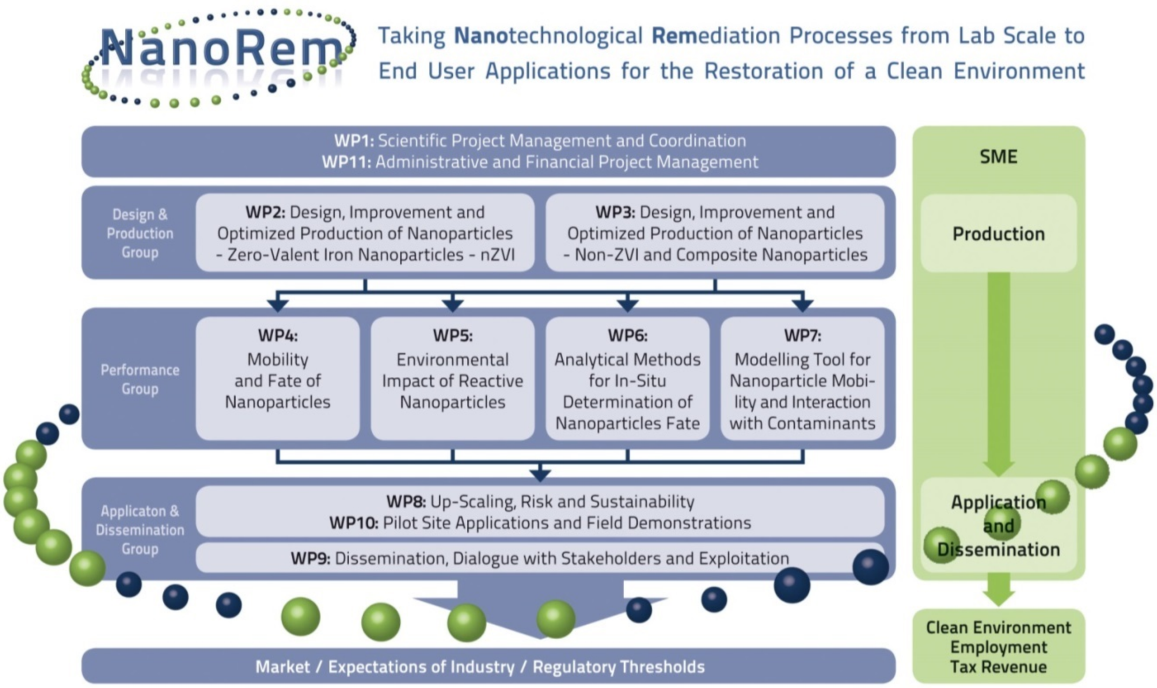

Figure 2: NanoRem's project structure

4 NanoRem Project Goals and Main Results

Six project goals were identified at the project outset. These are listed below along with a brief text describing how these goals were met.

Goal (1) Identify the most appropriate nanoremediation technological approaches to achieve a step change in remediation practice.

Model systems (NPs + conditions mimicking real environmental conditions), both existing and novel, have been used to investigate mobility, reactivity (destruction, transformation or sorption of contaminants), functional lifetime and reaction products. For NP optimization the influence of size, surface chemistry, structure and formulations on the performance were investigated leading to enhanced NPs as well as novel NP types. The step-change focus was to extend the range of practically treatable contaminants.

✓ Available NPs are listed in Table 1 and Table 2, some examples are shown in Figure 3. More information can be found within the Bulletin No 4 "A Guide to Nanoparticles for the Remediation of Contaminated Sites" and at www.nanorem.eu.

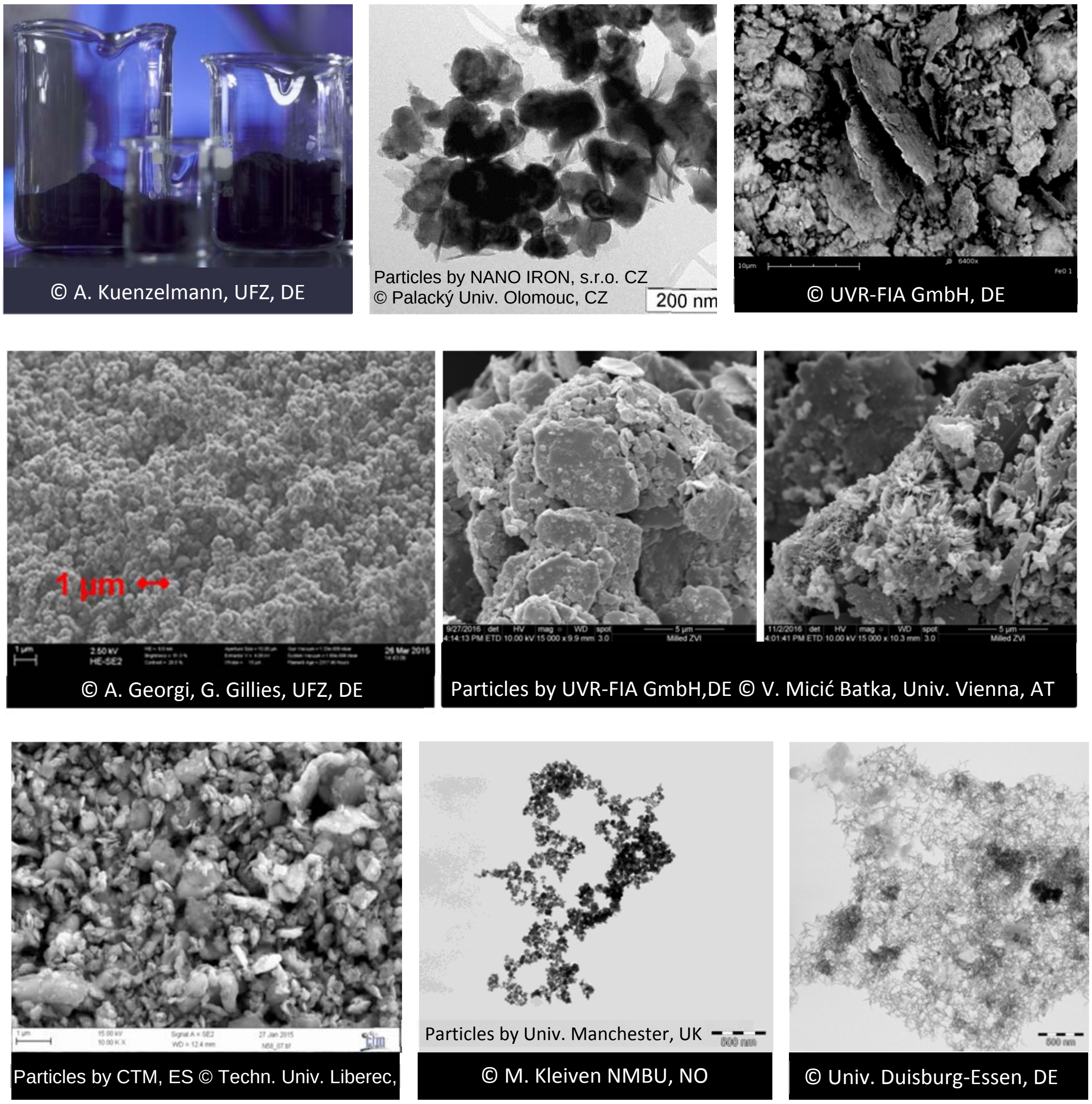

Figure 3: Different NPs from left to right: upper row: Carbo-Iron®, NANOFER (nZVI), milled nZVI particles; middle row: Trap-Ox Fe-zeolites, milled nZVI particles; lower row: milled nZVI particles, palladized bionanomagnetite, Nano-Goethite

Table 1: Commercially available NanoRem Particles

Particle name	Type of particle	Manufacturer	Process of contaminant removal	Target contaminants
Carbo-Iron® (industry)	Composite of Fe(0) and activated carbon	SciDre GmbH, Germany	Adsorption + Reduction	Halogenated organics (contaminant spectrum as for NZVI)
FerMEG12	Mechanically ground nZVI particles	UVR-FIA GmbH, Germany	Reduction	Halogenated hydrocarbons
NANOFER 25S	Nano scale zero valent iron (nZVI)	NANO IRON s.r.o., Czech Republic	Reduction	Halogenated hydrocarbons and heavy metals
NANOFER STAR	Air stable powder, nZVI	NANO IRON s.r.o., Czech Republic	Reduction	Halogenated hydrocarbons and heavy metals
Nano-Goethite	Pristine iron oxides stabilized with HA	University of Duisburg-Essen, Germany	Oxidation (bioremediation) + Adsorption of HM	Biodegradable (preferably non-halogenated) organics, such as BTEX; heavy metals

Table 2: NanoRem Particles under Development

Particle name	Type of particle	Manufacturer	Process of contaminant removal	Target contaminants
Trap-Ox Fe-zeolites	Nanoporous alumosilicate loaded with Fe(III)	UFZ Leipzig, Germany	Adsorbent + Oxidation (catalyst)	Small molecules (dep. on pore size of zeolite) - e.g. BTEX, MTBE, dichloroethane, chloroform, …
Bionano-magnetite	Produced from nano-Fe(III) minerals	University of Manchester, UK	Reducing agent and adsorption of heavy metals	Heavy metals, e.g. Cr(VI)
Palladized bionano-magnetite	Biomagnetite doped with palladium	University of Manchester, UK	Reduction (catalyst)	E.g. Halogenated substances (contaminant spectrum broader than for nZVI)
Abrasive Milling nZVI	Milled iron	Centre Tecnològic de Manresa, Spain	Reduction	Halogenated aliphatics and Cr(VI)
Barium Ferrate	Fe(VI)	VEGAS, University of Stuttgart, Germany	Oxidation	BTEX?, nitroaromatic compounds? (under investigation)
Mg/Al particles	Zero valent metals	VEGAS, University of Stuttgart, Germany	Reduction (reagent)	Halogenated hydrocarbons
Nano-FerAl	Composite of Fe and Al	UVR-FIA GmbH / VEGAS, Germany	Reduction (reagent)	Halogenated hydrocarbons

Goal (2) Develop lower cost production techniques and production at commercial scales of nanoparticles.

Laboratory scale production processes were upscaled to the industrial level. The step-change focus was to produce substantially cheaper and more sustainable NPs.

✓ The production was upscaled successfully resulting in a commercially available and economically competitive technology.

- ✓ Nano-scale zerovalent iron particles (nZVI) have been improved via a new surface coating so that they are available as an air-stable dry powder in spite of a large specific surface. This allows for a more convenient handling (transportation to the site, storable). More information can be found within the Bulletin No. 4 “A Guide to Nanoparticles for the Remediation of Contaminated Sites” and at: www.nanorem.eu.

Goal (3) Determine the mobility and migration potential of nanoparticles in the subsurface, and relate these to their potential usefulness and also their potential to cause harm.

Experiments for mobility and migration potential ranged from laboratory scale (columns), over large-scale contained laboratory systems to field tests. Furthermore, investigations included unintended secondary effects of NPs application on environment and ecosystems (Fig. 4).

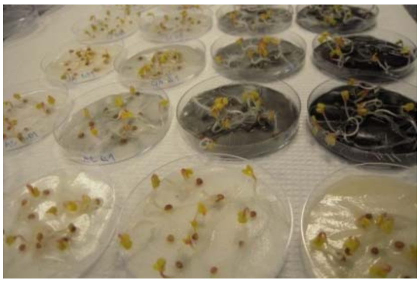

Figure 4: Nanoparticles developed during the project were tested for their potential effects on plant root elongation. The picture shows an overview of the test after a 6-day exposure of radish seeds *Raphanus sativus* to (from front to back) Fe-Zeolite, activated carbon, aged Carbo-Iron®, and Carbo-Iron® at 0.01, 0.1, 1 and 10 g/L. © Claire Coutris, NIBIO, Norway

- ✓ All NPs were intensively tested and optimized with respect to *mobility* and *reactivity* in column experiments; the three nZVI particles, Carbo-Iron® and Nano-Goethite additionally in large scale experiments and at different field sites. In lab-scale studies, the migration potential of some types of NPs was optimized by using special additives. Other NPs types were shown to form stable suspensions as delivered by their producers.
- ✓ Further information on “*Stability, Mobility, Delivery and Fate of optimized NPs under Field Relevant Condition*s” can be found in the respective project deliverable.
- ✓ *Large Scale Experiments* (LSE, Fig. 5) transferred the results from the lab scale (homogeneous condition) to technical scale (homogeneous or controlled heterogeneous condition). For more information, please see goal (6).

Figure 5: Large scale flume (LSF) experiment, University of Stuttgart, © VEGAS, Germany

- ✓ With regard to ecotoxicological aspects it was found that no significant toxic effects were observed on soil and water organisms when ecotoxicological tests were undertaken for a range of nanoparticles available for remediation (including with respect to the particles' interaction with contaminants and the resulting products).
- ✓ A suite of standard and non-standard ecotoxicity tests, covering both terrestrial and aquatic organisms, did not lead to any hazard classification according to EU regulation for any of the tested particles. All particles, except the FerMEG12, can be considered non-toxic to organisms living in aquatic and terrestrial ecosystems. Effects on selected soil and water organisms were monitored for up to one year after NP injection at the pilot sites. In three out of four sites, no toxic effects were observed. A temporary increase in toxicity was observed right after NP injection at only one pilot site. More information can be found at www.nanorem.eu.

Goal (4) Develop a comprehensive set of tools for design, application and monitoring practical nanoremediation performance and determine the fate of nanoparticles in the subsurface.

The bulletins and tools described below can be downloaded from www.nanorem.eu.

- ✓ *Appropriate Use of Nanoremediation* (Bulletin No 2). The aim of this "position paper" is to provide a concise and easily read overview of NanoRem's views on the appropriate use and application of nanoremediation technologies, and provide some clarity about how they are regulated in comparison with other forms of *in situ* reduction and oxidation remediation technologies.
- ✓ The *Generalised Guideline for Application* (Bulletin No 3 and Tool) gives a comprehensive overview on the implementation of nanoremediation. The aim of this guideline is to assist practitioners and consultants in screening nanoremediation as a possible remediation option for a given site and facilitate the communication between regulators and consultants.
- ✓ Numerical tools for *Forecasting NP Transport for Soil Remediation* (Bulletin No 6) include a 1D modelling tool (MNMs)[1] for the assisted quantitative analysis of laboratory-scale column tests and the preliminary design of pilot NP injections in simplified geometry (radial 1D simulations), and a full 3D transport module (MNM3D)[2] for the simulation of particle injections (in one or more injection points) in heterogeneous domains and prediction of NP fate and transport at the field scale. The Bulletin gives details on how the tools can support the various stages of the design, implementation and evaluation of a nanoremediation.
- ✓ Analytical methods and field measurement devices (Bulletin No 5 "Monitoring Methods") are needed to follow the fate of nanoparticles during and after a injection, and to evaluate the efficiency of remediation. A variety of methods have been developed and tested at NanoRem field injections, ranging from on site sampling and measurement to in situ tracking using magnetic susceptibility (Fig. 6).
- ✓ The *Risk Screening Model* (Tool) is used to establish whether NanoRem particles can be injected without causing pollution of groundwater or surface water.

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[1] **M**icro- and **N**ano-particles transport, filtration and clogging **M**odel **S**uite, www.polito.it/groundwater/software
[2] **M**icro and **N**anoparticle transport **M**odel in 3D geometries
Bianco, C., Tosco, T., Sethi, R. (2016) A 3-dimensional micro- and nanoparticle transport and filtration model (MNM3D) applied to the migration of carbon-based nanomaterials in porous media. *Journal of Contaminant Hydrology, 193, pp. 10-20*. DOI: 10.1016/j.jconhyd.2016.08.006

Figure 6: Preparation of the monitoring equipment at the Spolchemie Site 1 © VEGAS, University of Stuttgart, Germany

Goal (5) Engage in dialogue with key stakeholders and interest groups to ensure that research, development and demonstration meets their needs, is most sustainable and appropriate whilst balancing benefits against risks.

The main focus was on ensuring that the research addresses real market and regulatory interests. Communicating findings regarding renegade particles and the relative sustainability of nanoremediation over the life cycle of a typical remediation project was vital. Information and knowledge was being shared widely across the Single Market so that advances in nanoremediation can be properly exploited.

- ✓ NanoRem's *Exploitation Strategy, Risk-Benefit Analysis and Standardisation Status* summarises NanoRem's findings regarding dissemination and exploitation.
- ✓ NanoRem applied an internationally recommended approach to the *Life Cycle Assessment* (LCA) on the production process of three nanoparticles. *Life Cycle Inventories* (LCI) and impact assessments were applied to the production process of three zero valent iron nanoparticles being used at the pilot sites. Results from the impact assessment show the steps in the process that have major environmental impacts, for example energy consumption during the production. However, the boundary of the study has not gone beyond the production premises.
- ✓ The *NanoRem Case Study Sustainability Assessment Background and Workbook* has two broad purposes: to provide a background and NanoRem context for sustainable remediation and to provide a procedure to carry out a qualitative sustainability assessment of the nanoremediation technologies to be used at the field test sites.

Goal (6) Carry out a series of full scale applications in several European countries to provide cost estimations and performance, fate and transport findings.

NPs were applied both into large-scale contained laboratory systems and during field trials on the pilot sites, to provide on-site validation of the results on a representative scale both in terms of the effectiveness of nanoremediation as well as the environmental fate of the NPs and their associated by-products.

- ✓ In *field pilot tests* (see Table 3) the LSE results were verified under 3D heterogeneous field conditions. NANOFER STAR, FerMEG12 and Carbo-Iron® led to a (partial) degradation of CHC sources. Nano-Goethite particles were shown to "polish" a remaining BTEX contamination (groundwater plume) after a primary source removal. In the field trials on the pilot sites, the results of the LSE were validated in terms of effectiveness of nanoremediation and with respect to the environmental fate of the NPs and their associated by-products. It could be shown that nanoremediation works if the appropriate particles are selected for the conditions present at the site. Further information about the sites is given in the Site bulletins.

- ✓ A description of the applications and results can be found in the Site Bulletins on www.nanorem.eu. All field trials within the project were carried out within a risk management regime for nanoparticle release that gained the required regulators approvals and included where necessary a pre-deployment risk assessment protocol. Qualitative sustainability assessments have been conducted in a retrospective sense for one of the Czech pilot sites and as part of a remediation options appraisal for a separate UK based case study.

Figure 7: Injection of FerMEG12 (nZVI) into the Solvay site © VEGAS, University of Stuttgart, Germany

Table 3: NanoRem Pilot Sites

Site	Country	Site Primary Investigator	Target Cont.	NP-Type	Reaction Principle	Aquifer
Solvay	CH	Solvay	CHC	FerMEG12 (milled nZVI)	Reduction	porous / unconfined
Spolchemie 1	CZ	Aquatest	CHC	NANOFER 25S / NANOFER STAR	Reduction	porous / unconfined
Spolchemie 2	CZ	Aquatest	BTEX	Nano-Goethite (Iron-Oxide)	Oxidation / microbial enhancement	porous / unconfined
Neot Hovav	IS	Negev, BGU	TCE, cis-DCE, toluene	Carbo-Iron®	Adsorption / Reduction	fractured
Balassagyarmat	HU	Golder	PCE, TCE, DCE	Carbo-Iron®	Adsorption / Reduction	porous / unconfined
Nitrastur	ES	Tecnalia	As, Pb, Zn, Cu, Ba, Cd	NANOFER STAR	Reduction	porous / unconfined

5 Comprehensive Results - NanoRem Bulletins

An overview and the main results are condensed in twelve NanoRem-Bulletins which introduce the reader to NanoRem's research and provide an easy-to-read and useful information source for problem owners, consultants and decision makers. They can be downloaded free of charge from www.nanorem.eu.

(1) Nanotechnology for Contaminated Land Remediation - Possibilities and Future Trends Resulting from the NanoRem Project

(2) Appropriate Use of Nanoremediation

(3) Generalised Guideline for Application of Nanoremediation

(4) A Guide to Nanoparticles for the Remediation of Contaminated Sites

(5) Development and Application of Methods for Monitoring Nanoparticles in Remediation

(6) Forecasting Nanoparticle Transport for Soil Remediation

(7)-(12) NanoRem Pilot Site-Bulletins

6 Project Results online – the NanoRem Toolbox

The NanoRem toolbox (Fig. 9) is available on the NanoRem Web site www.nanorem.eu.

Figure 8: NanoRem website www.nanorem.eu

The NanoRem Toolbox (Fig. 9) focuses on the needs of decision makers, consultants and site owners. It provides the respective output of NanoRem in three levels:

(1) The bulletins include the most relevant information in a condensed and concise way.
(2) More detailed information on nanoparticles and tools are located in the "Nanoparticles and Tools" shelf.
(3) Other dissemination products and selected project deliverables can be found in the "Supporting Information" shelf.

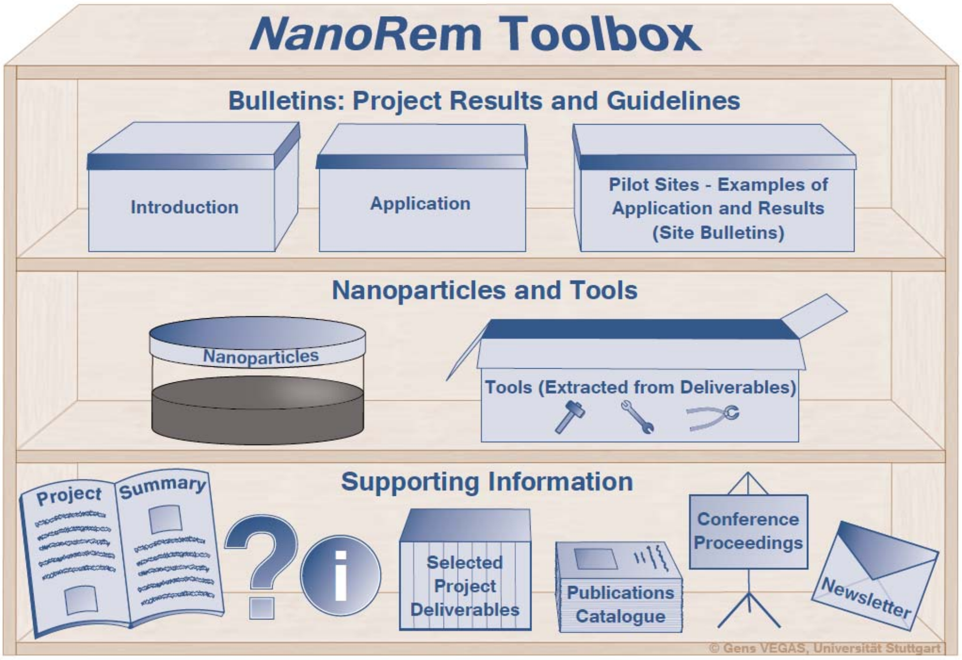

Figure 9: NanoRem Toolbox © VEGAS, University of Stuttgart, Germany

Figure 10: Project partners

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