Materials and Nanotechnology

Introduction

The focus of the Materials and Nanotechnology Program is materials technology development related to processing, analysis, testing and characterization, in general. These are achieved through execution of R&D projects in materials science and engineering as well as collaborative projects with private / public sector companies, universities and other research institutions.

Besides technology development, one other objective of this Program is modernization of existing facilities to be more competitive and to explore new opportunities. This Program also fosters training and human resource development in relevant areas in association with universities and specific industrial sectors.

The Materials and Nanotechnology Program is divided into sub-programs in the following areas: Ceramic Materials, Composite Materials, Metallic Materials, Physical / Chemical Characterization and Nanomaterials. The sub-programs are further divided into broad topics in research, development and innovation. Within each topic, several R&D projects are carried out.

Highlights of this program include:

- Calcium phosphate based macro-porous ceramics;
- Glass matrices to contain industrial and radioactive wastes;
- Glass microspheres for radiotherapy;
- Porous biomedical alloys;
- Processes to recycle industrial wastes into chemically resistant silicate glass based ceramics;
- Solid oxide fuel cell materials, components and unit cells to produce energy from different fuel sources;
- Proton conductors like barium cerate;
- Titanium and strontium based ceramics as oxygen sensors;
- High temperature erosion-oxidation resistant nanostructured coatings;
- Chromium-free corrosion resistant coatings for aluminum alloys;
- Thin film nanocrystalline structures, nanowires and nanotubes;
- Intermetallic compounds by combustion synthesis;
- Sintered components for use as cutting tools and filters;
- New classes of permanent magnets;
- Environment friendly nickel-metal hydride batteries;
- Sintered parts for the automotive industry;
- Processes to recycle zirconium alloy machining chips;
- X-ray diffraction reference materials;
- Residual stress measurement techniques;
- Copper based electrical components;
- Cyclic and monotonic testing of materials.

High temperature degradation resistant materials and coatings

The high temperature erosion-oxidation (E-O) behavior of several alloys and coatings have been studied in a E-O test rig. Erosion-oxidation maps of many coatings and alloys have been plotted to aid in material selection and include; (a) steels like AISI 1020, 410, 304 and 310; (b) HVOF coatings of Ni20Cr, Cr_3C_2 and WC-Co. Nanocrystalline coatings of a variety of oxides of rare earths (Dy, Er, Ce, Sm, Y, La, Pr and Nd) have been prepared to improve high temperature oxidation resistance of chromium dioxide and alumina forming alloys. Other nanostructured coatings have been prepared and studied. These include titanium dioxide nanotubes and HVOF deposited Cr_3C_2-Ni20Cr and WC-Co.

Corrosion resistant coatings

The automobile and aeronautics industries currently use conversion coatings for corrosion protection of steels and aluminum alloys. There are increasing restrictions to the use of these coatings due to toxicity. Hence, other alternate surface treatments are being tested and these include the use of self-organized monolayers - SAM. The surface treatment of aluminium alloys using this chrome-free SAM process is presently being studied.

Corrosion behavior of biomaterials

The corrosion behavior of metallic materials for use as implants was studied. The corrosion resistance of different alloys and coatings are being investigated and these include: Ti alloys, AISI 316 L stainless steels (with and without coatings), special austenitic stainless steels with high N content, PVD coatings and bioceramic coatings obtained by ion beam deposition.

Surface treatments for protecting carbon steels

The effect of modifications to the phosphating process to obtain coatings with improved corrosion resistance is being investigated. Also, currently under study are corrosion inhibitors for carbon steels used as reinforcement in concrete structures.

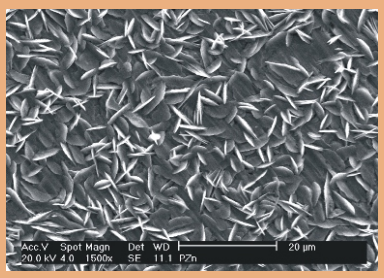


Figure 1. Scanning electron micrograph showing the phosphate layer obtained by surface treatment to protect carbon steels

Materials and technologies for a self-sustained environment

The main activities are related to the use materials science and technology for industrial process development with the aim of solving final waste problems. These include production control, inertizing, recycling or incorporation of industrial wastes in materials with increased economic value. The focus of the study included several industrial wastes like slags from metallurgical industries, residues from aluminum extraction plants, construction and demolition wastes. One other study focused on the recovery of platinum from fuel cells. Green stoneware tiles have been produced by incorporating galvanic wastes in industrial mixes containing kaolin clay, feldspar, quartz and recycled domestic glass. The process that was developed allows the incorporation of up to 20 mass% of metal waste for effective immobilization in a porcelain matrix and it also contributed towards coloring the matrix. The material obtained revealed a high chemical resistance. The microstructure observed in the FESEM micrographs was obtained after chemical etching and the crystalline phases contract from the glass matrix. In another study, the effect of the presence of white dross residue (WDR), produced during aluminum recovery from slag in the formation of glass-ceramic frits used in ceramic glazes was determined. Fig. 2.

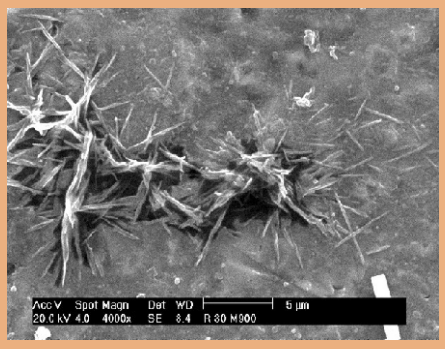


Figure 2. Fritted glass produced with 30 mass% WDR

Applied crystallography

Standard materials were developed for use as references in the calibration and determination of instrumental parameters of equipments used in diffraction (conventional X-rays, synchrotron and neutrons). The following standard materials for diffraction were produced: silicon (Si), yttria (Y_2O_3), lanthanum hexaboride (LaB_6), α-alumina (Al_2O_3), ceria (CeO_2), hydroxyapatite, silicon nitride and others. These are currently being evaluated for use for SAXS, XAFS and for in situ measurements under high hydrostatic pressures. The first set of samples were tested in other institutions and at Brazilian universities and these have shown excellent results.

Biomaterials

Research and development is being carried out on several general topics and these include bio-inert, bio-active or re-absorbable ceramics and new biomedical alloys. Nanometric hydroxyapatite powders, tricalcium beta-phosphate were developed by the neutralization method with variation of several parameters and using ultrasound. This led to obtaining nanometric materials and the incorporation of cations and anions in the crystalline structure of the materials. The repair of bone defects was evaluated with these materials by conducting in-vivo tests in Rattus norvergicus. Histological evaluation indicated that bone repair was successful. Calcium phosphate ceramics were obtained either in the dense or macroporous form. The latter was obtained by the direct consolidation method using albumin. (Fig. 3) In-vitro tests of these materials were conducted. Adhesion and cellular proliferation as well as initial biocompatibility were observed. The anchoring behavior and proliferation of fibroblasts was investigated on the surface of the ceramic specimens prepared with different surface treatments. The dissolution behavior of calcium phosphate based ceramics with different microstructures in simulated body fluid - SBF medium and a cell culture medium (DMEM) has been studied. The reactivity in SBF medium was investigated and the biocompatibility in culture medium with osteoblasts obtained from the bones of newly born mice. The in-vitro results indicated that the materials were biocompatible and did not reveal cellular death, or drastic morphological alterations that could compromise the metabolism of the cells.

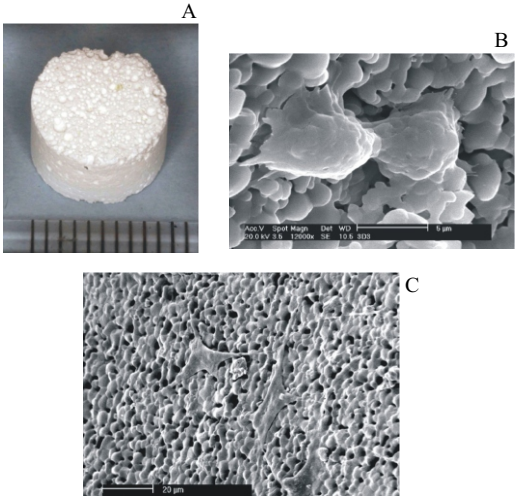


Figure 3. Scanning electron micrographs showing: (A) a macro-porous calcium phosphate based ceramic obtained using the albumin consolidation method; (B) osteoblasts originated in in-vitro culture test; (C) fibroblasts adhering to the ceramic surface in in- vitro test

Biomedical alloys

Ti13Nb13Zr alloy implants were obtained by the hydride route via powder metallurgy. The implants were then sterilized and surgically placed in the central region of rabbit's tibiae. Two double fluorescent markers were included and after an 8-week healing period, the implants were retrieved, non-decalcified sectioned and studied. The results indicated biocompatibility and osteoconductive properties of Ti13Nb13Zr processed by the hydride powder route.

Glasses

Glasses are being developed to immobilize industrial and nuclear wastes, to produce microspheres for radiotherapy treatments, and for other optical, electrical, and mechanical applications. A mathematical model using the Monte Carlo Method is being developed to determine the dose distribution in a human liver when neutron activated glass microspheres are directly injected in the organ through an artery. The purpose is to develop a fast, precise, and safe way to eliminate tumors in the liver.

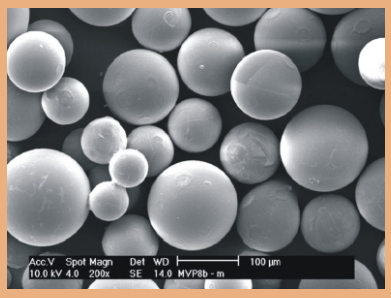


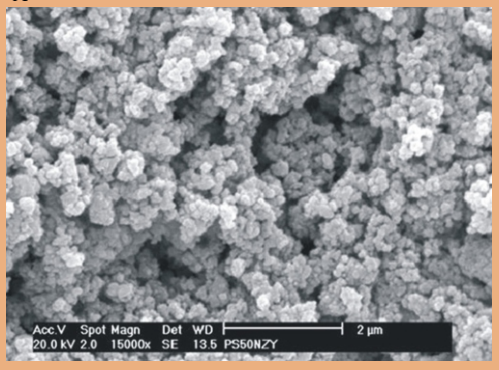
Figure 4. Glass microspheres containing phosphorous

Synthesis, processing, production and testing of SOFC unit cells

The properties of ceramic materials are strongly influenced by the chemical and physical characteristics of raw powders, such as particle size, surface area, chemical homogeneity and extent of agglomeration. Preparation of zirconia, rare earths, titania, alumina and silica based ceramics powders was done using various routes like powder mixture, co-precipitation, modified Pechini method, hydrothermal treatment and combustion synthesis. A scanning electron micrograph (SEM) of ZrO_2/NiO powder synthesized by co-precipitation is shown in Fig. 5a. Processing of high performance ceramic materials from the powders described above are done by milling,

classification and forming of ceramic bodies using techniques such as uniaxial and isostatic pressing, slip casting, tape casting, electrophoretic deposition and wet powder spraying. A SEM of the fracture surface of the electrophoretically deposited yttria stabilized zirconia (YSZ) layer on YSZ/Ni substrate is shown in Fig. 5b. and Fig. 5c a SEM of the cross section of strontium doped lanthanum manganite (LSM) deposited by wet powder spraying on YSZ electrolyte.

A



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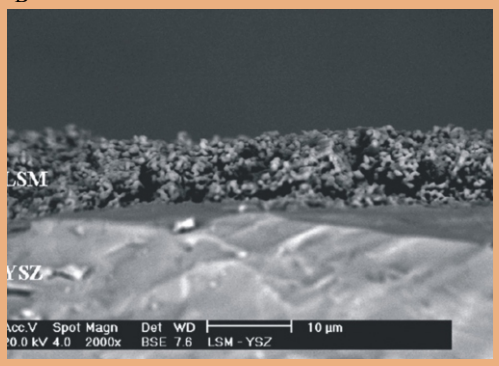

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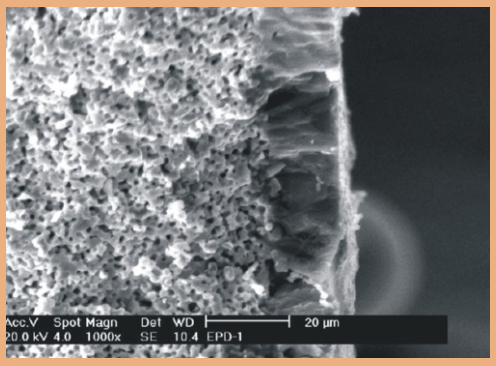


Figure 5. (A) ZrO_2/NiO ceramic powder synthesized by co-precipitation; (B) Electrophoretically deposited YSZ layer on ZrO_2/Ni substrate; (C); LSM layer wet powder sprayed on ZrO_2/Ni substrate

Electroceramics

Basic research work is currently focused on zirconia/ceria based ionic conductors and cerate / zirconate based proton conductors, particularly for the development of solid oxide fuel cells and oxygen sensors. The synthesis of ceramic nanopowders is carried out by several techniques: co-precipitation, using polymeric precursor, combustion synthesis and with polyacrylamide. The characterization of the powders is carried out by in-situ high temperature x-ray diffraction, thermal analysis and Fourier transform infrared absorption spectroscopy. Ceramic pieces are prepared by pressing and sintering. Conventional as well as fast firing and two-step sintering procedures are performed to obtain electro-ceramics with improved electrical properties. Electrical measurements are done using impedance spectroscopy at a wide range of temperatures (LNT-1500 K) and oxygen partial pressures (10 ppm-1 atm). Microstructure evaluation is carried out using x-ray diffraction analysis, scanning and transmission electron microscopy and Raman spectroscopy. Current technology development work consists of: (a) operation of solid oxide fuel unit-cells with proton and oxide ion conductors under hydrogen, methane and ethanol; (b) testing oxygen lambda sensors. In the period 2005-2007, the main results were:

- Development and testing of anode-supported solid oxide fuel cells with slurry-coated electrolyte and cathode under ethanol and hydrogen;
- Impedance spectroscopic evaluation of sintering of zirconia-yttria ceramics;
- Development of zirconia:magnesia-zirconia:yttria composites for high temperature oxygen sensors;
- Determination of the effect of additives on electrical performance of ceria-based materials;
- Synthesis of nanostructured zirconia - and ceria-based solid electrolytes.

Ceramics

Advanced materials have tailored microstructures for specific applications in high technology industries. Among the many applications of advanced ceramics, cutting tools are prominent and these require specific properties such as high chemical stability, thermal shock resistance, high hardness and wear as well as tear resistance. Among the ceramic materials that have been developed, the more important ones are those based on silicon nitride, silicon carbide, zirconia and alumina. These ceramic materials are processed by different routes to achieve high relative densities and optimized microstructures to increase fracture toughness, a property considered important for the ceramic materials. When

Alumina based composites, with niobium carbideadditions had their performance evaluated during machining of vermicular cast iron, the ceramic tools suffered abrasion and adherence, but presented acceptable performance under operating conditions. Acid attack of Si_3N_4 ceramics was studied to evaluate their potential use in aggressive atmospheres. Inorganic polymers play an important role in the processing of ceramic materials, either as an additive for forming parts or as a ceramic precursor. Polymer precursors enable, with appropriate treatments, different types of ceramics to be obtained and from which the removal of the precursor is not essential. The effect of adding polysiloxane as a precursor on the microstructure of alumina has been studied. The preparation of ceramic composites using small amounts of polymeric precursors indicated this method to be a simple and viable route to produce pieces containing refractory phases and with complex geometries. Fig. 6.

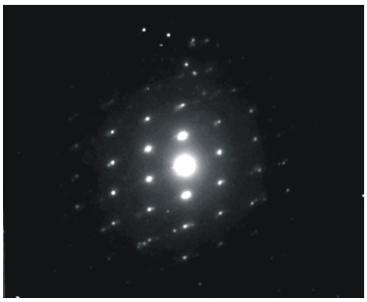


Figure 6. Electron diffraction pattern of the phase $Si_2Al_4O_4N_4$

Micro and nanostructured coatings

A metal-organic chemical vapor deposition (MOCVD) system was installed to develop micro and nanostructured coatings. The MOCVD technique is an extension of the CVD technique and enables the deposition of several metals and ceramics. Currently this system is being used to: (a) develop nanocrystalline deposits of TiO_2/TiNO and of Y_2O_3 on mono and polycrystalline substrates; (b) prepare nanostructured fine films and three-dimensional nanocrystalline structures such as nanofibres and nanotubes.

Synthesis using mechanoactivated combustion

The purpose of this project is to verify the influence of high energy milling on combustion synthesis of intermetallic compositions such as niobium tri-aluminide, $NbAl_3$. Milling is used to prepare mixtures of the powders of the constituent elements of the intermetallic compound, mainly to promote an intimate mixture and to reduce the particle size of the reactants (mechanical activation). The combustion is accomplished in compacted tablets of the mixture previously processed by grinding. Funding obtained enabled improvements in existing infrastructure, mainly to expedite characterization of the processed materials and for the construction and operation of a system to study hydrogenation/ dehydrogenation of materials.

Polymer matrix composites

One of the projects in this area is related to the construction of a hybrid composite material tube with carbon and glass fibers, for use as a prosthetic extension of lower limbs and to be eventually manufactured for the Association for the Assistance of the Impaired Children - AACD. The aim was to evaluate and optimize cost and to reduce weight. Finite element modeling was used to optimize the component in terms of bio-mechanical functions required of a prosthesis. This modeling took into consideration the amount of material, number of layers as well as other requirements to minimize cost. A survey resulted in finding a cheaper route to manufacture the composite using the vacuum assisted resin transfer molding (VARTM) process and pre-forms of glass with carbon. A patent application has been submitted. In order to compare the quality of the composite tube, another tube was produced using the conventional filament-winding process. Currently the VARTM process relies on imported feedstock. Even though some of the properties of the VARTM composite tube require further improvement, overall it presented advantages such as weight reduction and increased impact absorption. (Fig. 7)

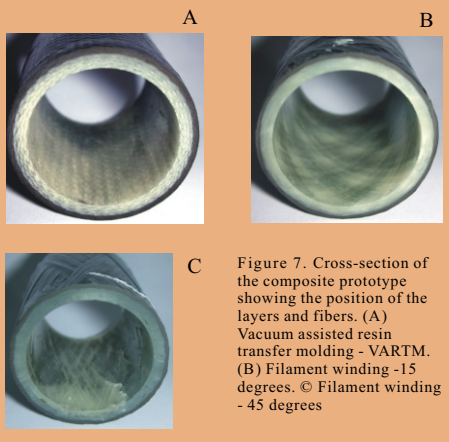


Figure 7. Cross-section of the composite prototype showing the position of the layers and fibers. (A) Vacuum assisted resin transfer molding - VARTM. (B) Filament winding -15 degrees. © Filament winding - 45 degrees

Powder metallurgy

Research and development of powder processing techniques. This involves support services for research and technology development in collaboration with industries, universities and other research institutions. Sintered components have been developed for applications as cutting tools, AISI M2 and T15 high-speed steels and filters. Samples of compacted stainless steel plates (80 x 140 mm and 2.0 mm thick) were prepared in collaboration with the company BRATS Special Materials.

Magnetic materials

R&D activities related to processing of metallic materials with rare earths using hydrogen technology and the powder metallurgy route. The microstructure and properties of magnetic alloys based on Sm-Co, Pr-Fe-B and Nd-Fe-B were studied. Nickel-metal-hydride based batteries (less aggressive to the environment than the lithium-cadmium batteries) are being developed with the alloys: La-Ni, La-Mg, La-Pr-Ni-Mg. Other activities include: processing of biomaterials with Y- or Nb-Zr alloys; development of uranium- molybdenum alloy powders for use in the nuclear area.

Recycling of Zircaloy

The production of fuel elements for the Brazilian Angra -I and -II PWR reactors involves machining of zircaloy tubes. A considerable amount of machining scrap are produced and since Brazil imports zircaloy a project to recycle zircaloy machining scrap was started. This project envisages development of the process to reuse Zircaloy scrap and consists of: adaptation of the vacuum arc remelt (VAR) furnace, melting, remelting or refining of consumable zircaloy electrodes using a non-transferable electric arc.

Figure 8. Macrograph showing a compact of stainless steel scrap and its consolidation in the VAR furnace

High-pressure cells

The purpose of this project is the specification and construction of a pressure cell for use in the Brazilian Synchrotron Light Laboratory - LNLS and in the IPEN neutron diffractometer. The objective was to initiate studies using the neutron diffractometer that is presently in the testing stage and for use eventually during the second semester of 2008. The design and construction of the pressure cell were based on the Paris-Edinburgh cell design. However, the new cell is lighter and more compact. As a consequence, the cell operates at lower pressures of up to 2 GPa. The design incorporates new materials that were developed at IPEN. A patent application for the design of the cell has been made. That cell will operate in the neutron diffraction facility installed in the IPEN research reactor, IEA-R1. The purpose is to provide the users the possibility of conducting neutron diffraction measurements on samples submitted to external hydrostatic pressures of up to 2 GPa.

The nanotechnology has been pointed as a high innovative technology allowing a deep and wide change in the materials production application. The molecular planning atomic in an atomic scale is a new technology concept starting that allows a new functionality of the matter. This leads to the control of the physical, optical, electronics, surface and magnetic properties and reactivity of the nanostructured functional materials. The nanotechnology is today one of the main points of the research activities, development and innovation in all of the industrialized countries. There are some nanotechnological products in the current market, but it will increase in a short time. That new technology concept has been at development at CQMA, by the study of nanostructured functional materials. The following activities are in development at IPEN:

Lanthanides supermolecules as fluoroimmnuoassays agent for desease detection. Prostate Specific Antigen (PSA)

Prostate cancer is the most common malignant tumor in men, corresponding to approximately 27% of all male cancer. In this work it is studied the use of lanthanide - diketonate supermolecules with macrocyclics as markers for prostate specific antigen (PSA) detection in serum sample. Most specifically it was studied the interaction, supermolecules/antigen/antibody by electronic spectroscopy (fluorescence/absorption) using compounds based on lanthanides as biological markers. It was made a fluoroimmunologic assay using these compounds that showed an efficient luminescence and physical chemical properties for acting as luminescent probe. In this method, the luminescent probe is chemically conjugated to an antibody, which link in a specific way with the biomolecule or organism. The luminescent probe is sensible to the chemical environment and its luminescence can indicate the presence of the biomolecule or organism. The supermolecules that showed high stability were tested as fluoroimmunoassay markers for tests of PSA in serum. It was established a routine methodology for PSA detection aiming to implantation of this kit in the Brazilian market. This work is supported by CNPQ-RENAMI and FAPESP agencies.

Magnetic nanoparticles and their application in biotechnology. Synthesis and characterization of $MnFe_2O_4$

Magnetic nanoparticles are of great technological importance because of their use in magnetic fluid, information storage system, medical diagnostics, etc. Various preparation techniques have been used for the synthesis of fine particles of ferrites, which exhibit novel properties when compared to their properties in bulk. Nonconventional methods such as co-precipitation, thermal decomposition, solgel and hydrothermal methods have been widely used. Ultra fine ferrite particles can be prepared by the simple chemical co-precipitation method. In this field spinel ferrites have received considerable attention because their magnetic properties can be varied systematically by changing the identity of the divalent Me^{2+} cations (Me = Co, Mn, Zn, etc.) without changing the spinel crystal structure. It was synthesized and characterized magnetic nanoparticles of manganese ferrites and this nanoparticles doped with gadolinium and covered with a biopolymer, chitosan for biological application. Some variable, as: pH of precipitation (11, 12 and 13), type of alkaline solution (NH_4OH, KOH, LiOH and NaOH), molar concentration of the solution, anneling time (0, 1 and 2 hours), the addition of surfactant in the solution of metals, gadolinium percent doped (1, 3, 5, 7 and 10% molar) were studied.

Figure 9. Magnetic nanomaterials

Metals recognition by smart supported liquid membranes (SLM)

Liquid membranes have been an emerging technique used as an alternative for the separation and pre-concentration of several metallic species. It have been applied as one alternative technique in the separation of metallic ions originating from several areas of industry like the hydrometallurgical, gases separation, biotechnology, treatment of nuclear and non-nuclear waste. The recovery of those metals through that technique has good potential to reduce, in very low levels, pollutants in processes. The liquid membrane is a solution, that is an organic solvent, water immiscible and with low dielectric constant, that is used as a diluent for an extractor agent, also called the sequestering agent, loader or metal transport, that is absorbed in the microporous of a polymeric film and actuates as solid support of the liquid membrane. The extractor agent gets the metallic ion from the feeding solution, liberating it on the other side of the membrane, through stripping solution. Then, the extraction and stripping of the metallic species are carried out in a single step in the process, and has this advantage in relation to the liquid-liquid extraction that requests a large number of stages to obtain products with high purity. It was investigate the influence of several parameters in the process of extraction of lanthanide metals and uranium originating from a simulated radioactive waste using as polymeric support membranes, PTFE and as loader calixarenes. The calixarenes are part of a very versatile class of macrocyclic compounds that can be functionalised, being obtained like this a great variety of multifunctional receptors.

Materials based on uranyl ion and their potential for solar energy conversion cells

The search for renewable sources of energy has led to an increasing interest in photochemical cells because of their possible role as transducers of solar to electrical energy. On the other hand uranyl compounds (UO_2^{2+}) present a great potential as luminescent materials, for instance, applied in technology laser, luminescent probes, cells for conversion of energy, etc. In this work it was studied two compounds of UO_2^{2+}based on methanessulphonate and calixarenes for to be used as efficient Light Conversion Molecular Devices (LCMD) and/or in solar cells for energy conversion. The uranyl ion possess some properties which make it a potential component for a solar energy conversion, that is, absorbs light in the shorter wavelength range of the solar spectrum, producing a relatively long lived excited state. The excited state has fluorescence peaking at ~520 nm, a property which makes it relatively convenient to investigate its reaction. The redox potencial of the excited uranyl ion makes a powerful oxidizing agent. This may be of potential use in the photogeneration of oxygen, which is of great importance for the photocleavage of water. Up to now we have investigated the electronic properties of some uranyl compounds (UO_2^{2+}).

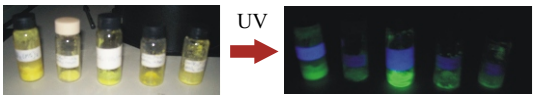


Figure 10. Uranyl Complexes as dye sensitized solar cells (DSSCs)

Preparation and spectroscopic study of nanoparticles of rare earth for biolabeling

The use of nanoparticles as labels in place of conventional molecular fluorophores has improved the biomolecular detection in terms of sensitivity and selectivity. A microwave method has demonstrated good results for preparing inorganic phosphor nanoparticle labels. The capping process adds a silane layers to the surface of the Y_2O_3:RE^{3+} (RE=Rare Earth) particles and provides amine groups for biological conjugation. Y_2O_3:RE^{3+} materials act as an inorganic phosphors with a spectrally narrow emission and a long emission lifetime. Y_2O_3:RE^{3+} phosphors are prepared by Pechini and combustion methods and functionalized with 3-aminopropyltrimethoxysilane (APTMS) using microwave technique. Determination of amino groups in Y_2O_3:RE^{3+} system is performed using a method involving ninhydrin. Luminescent properties of functionalized and unfunctionalized compounds are very similar.

Luminescence of natural polymeric magnetic films based on chitosan and lanthanide β-diketonate compounds

Chitosan is the deacetylated form of chitin, which is a linear polymer of acetylamino d-glucose. Recently, chitosan that is used as an adsorbent has drawn attentions due to its high contents of amino and hydroxy functional groups showing high potentials of the adsorption of dyes, metal ions and proteins. Other useful features of chitosan include its abundance, non-toxicity, hydrophilicity, biocompatibility, biodegradability and anti-bacterial property. In this work we investigate the properties of a film based on chitosan doped with ß-diketonate of europium. These films are candidates to be used as biosensor or in displays. The chitosan films were synthesized using a solution of chitosan in acetic acid and an alcoholic solution of $Eu(TTA)_3 2H_2O$ in weight proportion (0.1%). For the magnetic film we use a manganese ferrite dispersed into the chitosan solution. The compounds were characterized by: thermogravimetry (TG),

differential scanning calorimetry (DSC) and infrared spectroscopy. The emission spectra of the Eu^{3+}-TTA complex doped in the chitosan films recorded at 298 and 77K exhibited the characteristic bands arising from the $^5D_0$-^7F_J transitions (J = 0,2,4). The experimental intensity parameter, Ω_2;(34, 24) for non magnetic and magnetic films respectively, indicated that the Eu^{3+} ion in the precursor complex is in a more polarizable chemical environment than in the magnetic and non magnetic doped films. The emitter $^5D_0$ level lifetimes for doped samples show the luminescence decay curve profiles of second order exponentials. It was observed suppression of luminescence for the material with ferrite nanoparticles. The emission quantum efficiency (η) equal to 35.3 and 13.11 for the non magnetic and magnetic films is also discussed.

Synthesis and characterization of inorganic ion exchangers based on tin-titanium mixed oxide to be used in recovery of cadmium and nickel

This work presents the synthesis, characterization and adsorption studies of inorganic ion exchangers based on tin-titanium mixed oxide for recovery of cadmium and nickel metals from aqueous effluents, discarded in the environment mainly through NiCd battery. The exchangers were synthesized by sol-gel modified method using a mixture of tin(IV) chloride and titanium (III) chloride and ammonium hydroxide, precursor reagents. The materials obtained: SnO_2/TiO_2 e SnO_2/TiO_2:Eu^{3+} were characterized by infrared spectroscopy, thermal analysis, scattering electronic microscopy (SEM), X-ray powder diffraction (XRD) and electronic spectroscopy (excitation and emission) for the europium doped exchanger. The same materials also were synthesized too in polymeric matrix and can be used in column, because the synthesized materials showed crystals size in nanometric scale. It was determined by the distribution ratios for metals taking as parameters the influence of pH, the concentration of metals (by adsorption isotherms) and the contact time. The inorganic ion exchanger presented high exchange capacity with adsorption percent above 90% for the studied conditions, heterogeneous exchange surfaces and physic adsorption. It was calculated Gibbs energy for the process of exchange and the results agree with a spontaneous process.

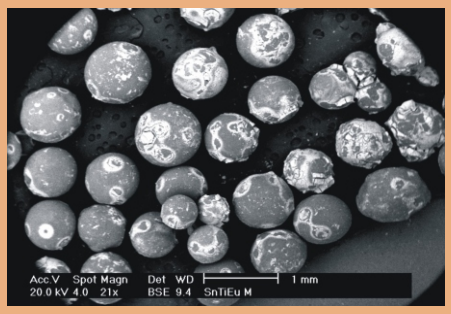


Figure 11. Inorganic ion exchange based on Ti/Sn oxide

Chitosan hydrogels membranes obtained by UV irradiation

Chitin, the second-most abundant natural polymer after cellulose, is the main structural component of marine crustaceans such as crab, krill, lobster and shrimp. Chitosan, a linear polymer of D-glucosamine, and the naturally unique alkaline polysaccharide, is easily obtained by alkaline N-deacetylation of chitin. In this work it was synthesized hydrogels based on chitosan biopolymer crosslinked by two-size polyethyleneglycol of different molecular mass PEG 300 and PEG 400 to be used in biotechnology applications. Those hydrogels were cured by two sources of energy γ-radiation (cobalt δ source with 25, 20, 15, 10 KGy and 60 Watts UV-radiation lamp). The hydrogels irradiated by cobalt source presented decomposition and were burned. For characterization, the hydrogels were dried until constant weight and analyzed by infrared spectra (IR), thermal analyses and UV absorption spectra The IR spectra of dried materials showed characteristic bands of chitosan, attributed to OH = and NH centered at 3446 cm^{-1}, Amide I band corresponding to C=O vibration (1650 cm^{-1}) of acetyl groups in chitosan. The band Amide III at 1332 cm^{-1}, due to combination of NH deformation and the CN stretching vibration and the band due to C-O at 1089 cm^{-1}. Thermal analyses (TGA/DTGA) showed three events of loss. Molecular absorption spectra in UV-vis showed large bands in visible line of spectra. All swelling behavior is plotted on the average of three trials. The swelling kinetics and time dependent-swelling behaviors of chitosan/PEG300 hydrogels was obtained in deionised water (pH 7) at 25 degrees. To observe swelling response of the chitosan/PEG hydrogels when exposed to different pH conditions, the hydrogels were emerged until equilibrium in an aqueous medium of pH 2, 4, 7 and 9 at 25°C. The hydrogels presented higher swelling content in acid medium.

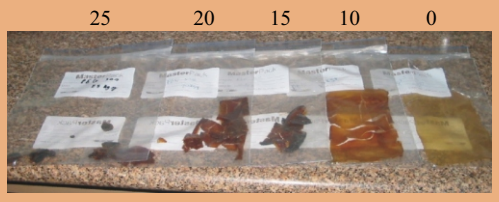


Figure 12. Decomposed membranes, UV spectra of UV irradiated membranes and their swelling behavior

Synthesis of superparamagnetic particles covered with chitosan for toxic and radioactive metals

Nanoparticles and the superparamagnetic particles possess a lot of applications in diverse areas of the human activities being, mainly in biotechnology and remediation of the environment. The superparamagnetic particles recovered by chitosan demonstrated to be good adsorbents of toxic metals and to other dangerous pollutants found in industrial effluents; therefore it was studied synthesis of such particles for coprecipitation in situ method and covering of the magnetic particles with chitosan methods by crosslinking in suspension, spray dryer and inversion of phases techniques. The particles had been characterized by transmission electron microscopy (TEM); scan electron microscopy (SEM), magnetization measurements, X-ray diffraction, infrared spectroscopy, condutimetric titration, termogravimetric analysis and differential scan calorimetry. The performance of recovered superparamagnetic particles with chitosan in adsorption of Cr (VI) and Th (IV) was studied from experiments carried out through bath system, using the kinetic models of external diffusion, diffusion intraparticles (Weber and Morris), pseudofirst order, pseudosecond order, models of Langmuir, and Freundlich and the hybrid Langmuir-Freundlich isotherms, and the thermodynamic parameters of adsorption.

Synthesis and characterization of magnetic cobalt ferrite nanoparticles covered with 3-amine propyltriethoxysilane for use as hybrid material in nanotechnology

Nowadays with the appear of nanoscience and nanotechnology, magnetic nanoparticles have been finding a variety of applications in the fields of biomedicine, diagnosis, molecular biology, biochemistry, catalysis, etc. The magnetic functionalized nanoparticles are constituted of a magnetic nucleus, involved by a polymeric layer with active sites, which ones could anchor metals or selective organic compounds. These nanoparticles are considered organic-inorganic hybrid materials and have great interest as materials for commercial applications due to the specific properties. Among the important applications it can be mentioned: magnetohyperthermia treatment, drugs delivery in specific local of the body, molecular recognition, biossensors, enhancement of nuclear magnetic ressonance images quality, etc. This work was developed in two parts: 1) the synthesis of the nucleus composed by superparamagnetic nanoparticles of cobalt ferrite and, 2) the recovering of nucleus by a polymeric bifunctional 3-amine propyltriethoxysilane. The products obtained were characterized using the following techniques X-ray powder diffraction (DRX), transmission electronic microscopy (MET), scanning electronic microscopy (MEV), spectroscopy of scatterbrained energy spectroscopy (DES), atomic emission spectroscopy (ICP-AES), themogravimetric analysis (TGA/DTGA), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and magnetization curves (VSM).

Titanium dioxide nanostructured films: characterization and nanotechnological applications

Nanoscience and nanotechnology are scientific-technological fields determined in understanding as the structural control of the matter at the molecular level can be used for the preparation of new materials with unique and exclusive properties. A very promising material for nanotechnological applications is titanium dioxide nanostructured films prepared by the sol-gel process and dip coating. The films are morphologically characterized for atomic force microscopy; crystalline phase and crystallite size for X rays diffraction spectrometry; optical properties for UV-VIS molecular spectroscopy. Our studies seek mainly to the improvement of the photocatalytic activity of titanium dioxide nanostructured films for development of solar cells with high efficiency conversion of energy solar in electric power.

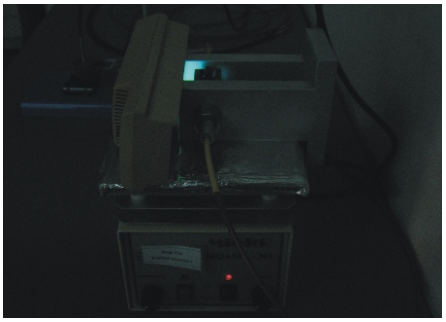


Figure 13. Photocatalytic activity evaluation of TiO_2 nanostructured films

Research project: zeolite-based nanostructured materials

Zeolite with highly regular, ordered cages and channels of nanometer scale is one of inorganic porous materials. The specificity, adsorption and catalytic properties of zeolites, besides the possibility of its pores to host different ions, atoms, molecules and clusters have opened up numerous opportunities of zeolites as advanced nanomaterials. The Brazilian coal ashes consist, basically, of aluminosilicate with high silicon and aluminium oxide contents. Since coal ashes are composed of a large amount of silica e alumina and also due to a low ratio SiO_2/Al_2O_3, they can be converted into zeolite by alkaline hydrothermal activation. Various types of zeolites can be obtained by changing the source of ashes or activation parameters. The zeolitic material obtained contains a non-converted part of coal ash and the zeolite content in the conversion product varies as a function of the coal ash properties and the conditions selected. Figure 14 shows the SEM (Scanning Electron Micrographs) images of zeolitic material synthesized from fly ash.

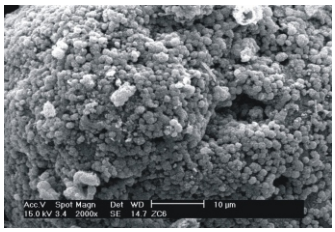


Figure 14. SEM photographs of zeolitic material synthesized from fly ash

The utilization of synthetic zeolites as adsorbent for the treatment of the electroplating effluents, immobilization of heavy metals in soil, decontamination of actual acid mine drainage and removal of dyes from aqueous solution has been evaluated. The results obtained in the project showed a great reduction in the pollutant concentration in treated waters and soil and demonstrated the high potential of the zeolites synthesized from Brazilian coal ashes as low-cost adsorbent nanomaterial for treatment of wastewater and soil.

Pt-Rare Earths/C electrocatalysts for PEM (Proton Exchange Membrane) fuel cells

Pt-Rare Earth/C electrocatalysts (Rare Earth = La, Ce, Pr, Nd, Sm, Tb, Dy, Ho Er, Tm and Lu) were prepared in a single step by an alcohol reduction process (developed at IPEN) using ethylene glycol as reduction agent and solvent and Vulcan XC 72 as support. The obtained materials (in the range of 6 to 15 nm) (Figure15) were tested for ethanol oxidation and oxygen reduction in acid medium using cyclic voltammetry and chronoamperometry. The X-ray diffractogram of Pt Rare Earth/C electrocatalysts showed the typical fcc structure of platinum and the presence of rare earth (III) hydroxides. All electrocatalysts showed higher current values than Pt/C in the potential range of interest for direct ethanol fuel cell (0.2-0.6 V). Further work is necessary to modify the electrocatalysts preparation methodology in order to decrease the Pt particle size and investigate these electrocatalysts in gas diffusion electrodes for tests in single direct ethanol fuel cell. (Project supported by CNPq)

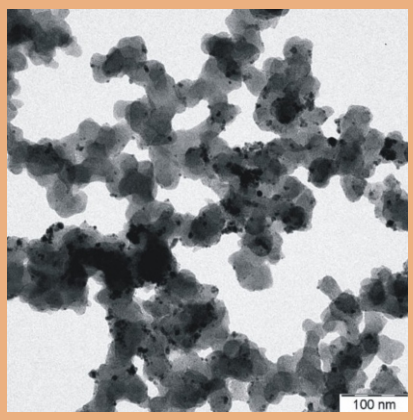
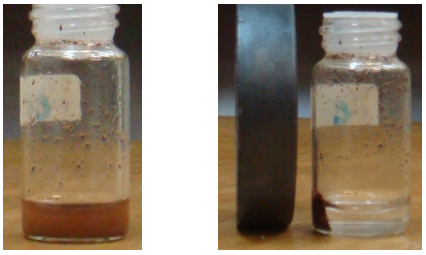


Figure 15. Transmission electronic micrograph (TEM) of Pt-La/C electrocatalyst prepared by the alcohol reduction method

Magnetic carrier technology as adsorbent

Synthetic magnetite has been prepared by precipitation process of the Fe^{2+} and Fe^{3+} ions with a basic solution. It is formed by nanoparticles and exhibit a strong magnetic response in presence of a magnetic field, without nevertheless becomes magnetic. The superparamagnetism, an intrinsic behavior of the magnetite nanoparticles, has been confirmed by magnetization measurements. The magnetite nanoparticles are good adsorbents of metallic ions and dyes and may be easily removed from wastewater using a magnet due to their superparamagnetic properties and as they do not hold a remanent magnetization, they can be disagrouped and reused after desorption of contaminants. The synthetic magnetite has been studied as adsorbent of U and Th ions from nitric solutions and has shown great perspective as an alternative adsorbent to conventional adsorbent. Another research focus has been

conducted for obtaining of magnetic carrier. The magnetite nanoparticles have been conjugated with adsorbent materials and organic complexants and their effect on enhancement adsorption capacity has been investigated. The technology of magnetic carriers for the wastewater treatment combines contaminant separation by sorption and magnetic recovery into a simple and compact process. Also called of magnetic adsorbent provides a simple way to remove contaminants from solutions under a wide range of chemical conditions. Dextran, citrate, chitosan, sugarcane bagasse and synthetic zeolite adsorbents were combined with the magnetite nanoparticles for obtaining of magnetic adsorbents.
Characterization and adsorption studies of U, Th, Cr ions and dyes Reactive Orange 16, Indigo Carmine and Congo Red were carried out. The sorption were studied by means of batch equilibrium, isotherm equilibrium, kinetic and Gibbs free energy. The equilibrium data were analyzed by the Langmuir and Freundlich isotherm models. The magnetic adsorbents of the chitosan and dextran presented the best results of adsorption of the U, Th, Cr ions and Congo Red dye. The Langmuir model was found to best describe the equilibrium isotherm data and the pseudo second-order model was found to explain the rapid kinetic of sorption. Recovery of 94% U from the magnetic chitosan by desorption process using carbonate ion was obtained. For all adsorption processes studied, the Gibbs free energy indicated the spontaneous nature and chemical adsorption. Magnetic zeolite was prepared by combination of magnetite nanoparticles and synthetic zeolite obtained from mineral coal fly ash. Under the studied conditions, about 80% of the Reactive Orange 16 dye and 42% of the Indigo Carmine dye were removed. The magnetic zeolite exhibited a potential application in treatment of textile wastewater as an efficient and low cost adsorbent for dye removal. Since 2006, the research project of magnetic zeolite has been supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico CNPq (proc. nº 472746/2006-Universal). Also, the magnetic bagasse was investigated for oil spill cleanup applications on water. This material absorbed the oil and was easily attracted by a magnet to remove it from water. The studies shown that magnetic bagasse may be used effectively in the area of oil spill cleanup. The majority of the sorbed oil was removed from the oil-saturated biosorbent by a simple mechanical compression suggesting that the biosorbent can be used repeatedly in oil spill cleanup. Further investigations on a more detailed analysis of the preparation of magnetic adsorbent by different methods and their application to the removal of heavy metals and dyes are in progress.



A B

Figure 16. (A) Magnetic chitosan suspension in an aqueous solution; (B) Magnetic separation of the magnetic chitosan from the aqueous solution

Development of HMS-PP to achieve high level of long chain branches (LCB)

Study of the radiation effect on the LCB formation on polypropylene (PP) of different molar mass (Mw), related to different values of melt flow index (MFI) has used acetylene and gamma irradiation. The linear viscoelastic behavior of these samples was investigated by an oscillatory rheometer. Melt strength and drawability were determined by Rheotens equipment. The melt strength of a polymer (maximum force at which a molten thread can be drawn under standard conditions before it breaks) is more efficiently achieved by addition of long chain branches (LCB). Gel permeation chromatography - GPC analysis reveals LCB on modified PP samples. The increase of melt strength of each HMS depends, in part, of the low level cross-linking achieved. But, the pronounced increase of the melt strength and drawability values confirms the presence of long chain branching resulted from the main radiation modification in presence of the acetylene monomer.

Research and development of a process to obtain high melt strength polypropylene (HMSPP) in the presence of liquids monomers

From this study it has been possible to develop two different routes to obtain high melt strength polypropylene (HMSPP) using high-energy radiation like gamma rays from ^{60}Co and pure homo polypropylene resin. In all processes to achieve HMSPP it was added up different quantity of liquids monomers. The monomers studied were ethylenoglycol dimethacryllate (Egdma), triallylcyanurate (Tac), triallyl-isocyanurate (Taic) and trimethylolpropane trimethacryalte (Tmptma) in range concentration of 0 - 5.0 mmoL/100 g of pure resin. The radiation process was carried out at room temperature and in two atmosphere conditions: one inert and another oxidative. It was analyzed the radiation doses of 10 and 20 kGy for both conditions. For all routes the samples were characterized by gel fraction, rheological properties, melt strength, extensibility and mechanical and thermal properties. From this project and using theses two kinds of process it was possible to produce HMSPP of different values of melt strength and consequently strain hardening.

Study of correlation between rheological parameters and processability of different modified polypropylenes

In this research it has been studied three kinds of high melt strength polypropylene (HMSPP) achieved by modification of polypropylene resin with gamma rays and polyfunctional monomer. Two HMSPP were obtained by polypropylene homo polymer with Tac. In the case of HMSPP achieved by random polypropylene copolymer (RP) it has been studied different kinds of RP with EVA blends. All HMSPP were characterized by rheological properties and submitted to thermoforming and expansion process.

Membranes to proton exchange

A membrane to perform as polymeric electrolyte has to have a combination of requirements in order to maintain good separation and electrochemical capabilities. These include high ionic conductivity, low swelling behavior, high chemical resistance and mechanical integrity. Many groups all over the world have studied commercial fluoropolymer films, which were irradiated, grafted with styrene and sulphonated. Projects of new membranes based on perfluoropolymers and polyolefin was developed using radiation-induced graft polymerization in presence of low molecular mass monomers. Grafting conditions are playing an important role when determining the degree of grafting and the structure built up inside the grafted polymer. In addition, the solvent used for monomer dilution is of special interest as it is one of the essential elements towards successful radiation-induced grafting processes. Solvents are usually used during grafting to bring about swelling of the base polymer, therefore increasing the monomer accessibility to the grafting sites. The PTFE, PP, PE among others are the polymer matrixes in which monomers are grafted in special solvent conditions. Simultaneous irradiation method used for membranes with sequential sulphonation of aromatic rings in order to introduce ionic groups that will be responsible for the proton transportation.

Biomaterials: drug delivery systems

Hydrogels from PVP were developed at IPEN to be used as wound dressings. Silicone and hydrophilic polymers like PVP, PVAl, PEG, CMC and others are being used to synthesize matrices for drug delivery systems (DDS). Controlled drug delivery occurs when a polymer, whether natural or

synthetic, is judiciously combined with a drug or other active agent in such a way that the active agent is released from the material in a predesigned manner. The purpose behind controlling the drug delivery is to achieve more effective therapies while eliminating the potential for both under- and overdosing. Other advantages of using controlled-delivery systems can include the maintenance of drug levels within a desired range, the need for fewer administrations, optimal use of the drug in question, and increased patient compliance. It has been developed hydrogel matrices as DDS for delivery of resveratrol, Assai berry oil, and the glycoprotein Antarticine for cosmetic purpose as well as silicone matrix with papain, prostaglandin (hormone therapy and induction of labour) and timolol for glaucoma treatment.

Natural polymers

Biodegradable foams from cassava starch were developed with partnership of CBPAK and this technology was transferred for this industry. Also biodegradable films were developed.

Organic-inorganic hybrid materials

Developments of membranes composed of hybrid materials are application of conceptual knowledge of nanoscience. Our group reported the synthesis and characterization of organic-inorganic hybrid materials based on Cassava starch (biopolymer) and Hectorite clay (a layer silicate). The materials were prepared by solution exfoliation process. In this method, layered clays are exfoliated into single platelets using a solvent in which the polymer is soluble. After the synthesis, the strong interfacial interaction between biopolymer and clay has been evidenced for homogeneous gels formed. The analysis of FTIR confirms the presence of the layered inorganic material and also two major polymeric components of the cassava: amylase and amylopectin. The thermogravimetric data show that the inorganic clay sheets delay the temperature of the biopolymer decomposition. When small amounts of clay are added, the PXRD data indicate the formation of exfoliated hybrid materials, in which the individual inorganic layers are separated in the polymer matrix. On the other hand, when great amounts of clay are added the intercalated hybrid materials are formed in a regular fashion, as a result of the polymer chains insertion into the layered inorganic structure.

Figure 17. Aerial view of the Materials Science and Technology Center (CCTM-acronym in Portuguese)

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