

**RAPPORTO FINALE SUI RISULTATI DEL PROGETTO COMUNE DI RICERCA  
FINAL REPORT ON RESULTS OF JOINT RESEARCH PROJECT**

**1. Accordo /Agreement**

CNR / SAV (Slovacchia)

anni/ years 2013-2015

**2. Titolo del progetto**

Sviluppo di processi innovativi per la valorizzazione di pile esaurite.

**2. Title of the project**

Development of Innovative processes for the valorization of spent batteries.

Parole chiave (massimo 3)

Processi innovativi, metalli pesanti, pile esaurite

Key words (max. 3)

Innovative processes, heavy metals, spent batteries

(solo per parte italiana)

Area scientifica / Scientific area (tabella 1/ table1)

Dipartimento Terra e Ambiente

**3. Responsabili del progetto  
Project leaders**

<b>Responsabile italiano</b> Dr. Stefano Ubaldini	<b>Slovak project leader</b> Dr. Alena Luptakova
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IGAG - CNR - IGAG		
Tit. .	Cl:	F:
N. 0002404	04/09/2015	



#### **4. Obiettivi del progetto**

Lo scopo del presente progetto, di cui si richiede il rinnovo per il biennio 2016 – 2017, era l’implementazione dei processi fisico-chimici (elettrochimici) e chimico-biologici (biolisciviazione e bioprecipitazione), basati sull’attività di batteri solfo-ossidanti, batteri solfo-riducenti e di altri microorganismi adatti (funghi microscopici e lieviti), al fine di sviluppare un processo innovativo per la valorizzazione di materie prime secondarie, cioè rifiuti quali batterie primarie scariche tipo Zn-carbone ed alcaline, per il recupero di valori metallici (Zinco) e per la produzione di altri componenti di interesse commerciale, quale il biossido di manganese.

Le attività sperimentali programmate all’inizio del triennio si prefiggevano di perseguire i seguenti obiettivi specifici:

1. Pretrattamenti e lisciviazione delle materie prime secondarie (pile esaurite);
2. Selezione e coltivazione di microorganismi adatti;
3. Pretrattamenti e biolisciviazione delle materie prime secondarie;
4. Purificazione della liscivia e produzione di componenti metalliche, sali e soluzioni per via chimica, chimico-biologica ed elettrochimica;
5. Trattamento dei reflui, analisi di processo integrata (tecnico-economica) di tutti i risultati ottenuti, analisi di impatto ambientale e Life Cycle Assessment (LCA) del processo.

L’obiettivo finale principale consisteva nello sviluppare l’analisi di fattibilità tecnico-economica dell’intero processo, con particolare attenzione alla qualità dei prodotti (elevata purezza per applicazioni tecnologiche) ed agli aspetti ambientali ed energetici.

#### **4. Aims of the project**

The purpose of this project, of which renewal is requested for the years 2016 - 2017, was the implementation of physicochemical processes (electrochemical) and chemical-biological (bioleaching and bioprecipitation), based on the activity of sulfur-oxidizing bacteria, sulfate-reducing bacteria and other microorganisms suitable (microscopic fungi and yeasts), in order to develop an innovative process for the valorization of secondary raw materials, such as primary exhaust batteries type Zn-carbon and alkaline, for the recovery of metal values (Zinc) and for the production of other components of interest commercial, such as manganese dioxide.

The experimental activities planned at the beginning of the three years aim to achieve the following specific objectives :

1. Pre-treatment and leaching of secondary raw materials (spent batteries);
2. Selection and cultivation of microorganisms suitable;
3. Pre-treatment and bioleaching of secondary raw materials;
4. Purification of leached solutions and production of metal components, salts and solutions, by chemical, chemical-biological and electrochemical way;
5. Treatment of waste water, process analysis integrated (technical and economic) of all the results obtained, environmental impact analysis and Life Cycle Assessment (LCA) of the process.

The ultimate goal was to develop an analysis of the main technical and economic feasibility of the overall process, with a focus on product quality (high purity for the technological applications) and to environmental and energy aspects.

## 5. Risultati ottenuti per obiettivo (1 pagina)

I principali risultati ottenuti attraverso il perseguitamento degli obiettivi, hanno portato all'ottimizzazione, su scala di laboratorio, di un circuito completo di processo articolato nelle seguenti fasi:

- 1) pretrattamento delle pile esaurite (operazioni meccaniche, di separazione fisica e di lavaggio) con la separazione primaria delle componenti di interesse sotto forma di polvere contenente Zn e Mn;
- 2) lisciviazione e biolisciviazione della polvere pretrattata per il recupero delle componenti metalliche sotto forma di soluzioni acquose e/o solidi;
- 3) purificazione della liscivia ottenuta con eliminazione di impurezze inficianti le proprietà chimiche e ferrimagnetiche dei componenti d'interesse;
- 4) produzione e caratterizzazione di ferriti secondo approcci combinati, utilizzando procedure chimiche, chimico-biologiche ed elettrochimiche;
- 5) trattamento dei reflui mediante tecniche convenzionali ed innovative (nano filtrazione a membrana, osmosi inversa e/o elettrodialisi, ultrafiltrazione, scambio ionico, adsorbimento, bioadsorbimento e bioprecipitazione).

L'analisi di processo integrata (tecnico-economica) di tutti i risultati ottenuti, l'analisi di impatto ambientale e Life Cycle Assessment (LCA) del processo, hanno dimostrato la **fattibilità tecnico-economica** dell'applicazione di un **circuito bio - idrometallurgico ecocompatibile** per il recupero **Zn e Mn** dalle **pile esaurite**.

Questo **processo innovativo** rappresenta un modo economico ed ecologico per il recupero dei metalli dalle batterie esaurite. I risultati evidenziano che il processo di biolisciviazione, condotto con *Acidithiobacillus ferrooxidans* isolato da acque acide di miniera (shaft Pech, Smolnik, Slovacchia Orientale) - integrato da tecnologie elettrochimiche - può essere utilizzato con successo nel processo di trattamento delle batterie alcaline.

In particolare, l'influenza della temperatura nel processo di biolisciviazione di Zn e Mn, è risultata essere determinante nel recupero selettivo dei metalli menzionati dalle batterie.

Alla fine della purificazione e conseguente deposizione elettrolitica dei prodotti finali di interesse, è stato raggiunto, su scala di laboratorio, un **recupero quantitativo (circa il 98 %)** di manganese ( $MnO_2$ ) e zinco disciolti in soluzione, mentre il **grado di purezza dei depositi elettrolitici è risultato superiore al 99%**.

## 5. Achieved results (one page)

The main results achieved through the pursuit of the objectives, led to the optimization, on a laboratory scale, a complete circuit of process articulated on the following phases:

- 1) pre-treatment of exhausted batteries (mechanical operations, physical separation and washing) with the primary separation of the components of interest in the form of powder containing Zn and Mn;
- 2) leaching and bioleaching of the powder pre-treated for the recovery of the metal components in the form of aqueous solutions and/or solid;
- 3) purification of the leaching/bioleaching solutions obtained, with elimination of impurities that interfere with the chemical and ferrimagnetic component of interest;
- 4) Production and characterization of ferrites according to combined approaches, applying chemical, chemical-biological and electrochemical procedures;
- 5) treatment of wastes by conventional and innovative techniques (membrane nano-filtration, reverse osmosis and/or electrodialysis, ultrafiltration, ion exchange, adsorption, bioadsorption and bioprecipitation).

The integrated process analysis (technical and economic) of all the results obtained, the environmental impact analysis and Life Cycle Assessment (LCA) of the process, demonstrated the **technical and economic feasibility** of applying a bio - hydrometallurgical **environmentally friendly circuit**, for recovering **Zn and Mn** from spent batteries.

This **innovative process** is an economical and ecological recovery of metals from spent batteries. The results show that the process of bioleaching, conducted with *Acidithiobacillus ferrooxidans* isolated from the acid mine drainage (the shaft Pech, the locality Smolnik, Eastern Slovakia) - integrated by electrochemical technologies - can be successfully used in the treatment of alkaline batteries.

In particular, the influence of temperature in the process of bioleaching of Zn and Mn, was found to be crucial in the selective recovery of mentioned metals from batteries. At the end of the purification and subsequent electrolytic deposition of the final products of interest, has been reached, on laboratory scale, a **quantitative recovery (about 98%)** of manganese ( $MnO_2$ ) and zinc dissolved into the solution, while the **degree of purity of electrolytic deposits was over than 99 %.**

## 6. Prodotti del progetto / Results obtained

	n./no.
Pubblicaz. scient. su riviste internaz./ scientific publications on international reviews con/with IF: 3 senza/without IF: 0	3
Pubblicaz. in atti congressi internaz./ publications in international congress proceedings	7
Pubblicazioni in atti congressi nazionali / publications in national congress proceedings	
Pubblicazione libri nazionali / Publication of national books	
Pubblicazione libri internazionali / Publication of international books	
Altre pubblicazioni / other publications	5
Brevetti / Patents	
Prototipi / Prototypes	
Strumentazione / Equipment and /or Devices	
Programmi software / Software	
Banche dati / Data bases	2
Protocolli / Protocols	
Nuovi Materiali / New Materials	
Nuovi processi / New processes	3
Cataloghi/inventari/repertori / Catalogues/Inventories	
Atlanti/Carte/Mappe / Atlases/Charts/Maps	
Progetti di ricerca / Reserch project	
Trasferimento innovazioni / Knowledge transfer	3
Laboratori congiunti / Joint laboratories	4
Alta formazione / Training	
Altro / Other	10

## **7. Informazioni dettagliate sui risultati indicati sub 6**

### ***Pubblicaz. scient. su riviste internazionali con IF:***

- 1) S. Ubaldini, J. Kadukova, A. Mrazikova, P. Fornari, A. Luptakova, R. Marcincakova, P. Pizzichemi. Application of innovative processes for the valorization of alkaline spent batteries, Chemical Engineering Transactions, ISBN 978-88-95608-30-3; ISSN 2283-9216, Vol. 39, pp. 1609-1614, 2014. DOI: 10.3303/CET1439269.
- 2) Eva Mačingová, Stefano Ubaldini, Alena Luptáková. Study of manganese removal in the process of mine water remediation, Journal of the Polish Mineral Engineering Society, ISSN 1640-4920, corso di stampa 2015.
- 3) R. Marcincakova, J. Kadukova, A. Mrazikova, O. Velgosova, A. Luptakova, S. Ubaldini. Metal bioleaching from spent lithium-ion batteries using acidophilic bacterial strains, Journal of the Polish Mineral Engineering Society, ISSN 1640-4920, in corso di stampa 2015.

### ***Pubblicaz. in atti di congressi internazionali:***

- 1) Stefano Ubaldini, Alena Luptakova, Maria Prascakova, Eva Macingova, Jana Jencarova, Possibilities of Bio-hydrometallurgical treatment of spent alkaline batteries, Proceedings of the 5th International Conference “Applied Natural Sciences 2015“, Jasná, Low Tatras, Slovak Republic, September 30 - October 2, in corso di stampa 2015.
- 2) Eva Mačingová, Stefano Ubaldini, Alena Luptáková. Study of manganese removal in the process of mine water remediation, Proceedings of the 19<sup>th</sup> Conference on Environment and Mineral Processing – Part I, ISBN 978-80-248-3753-6, pp. 61-66, Edited by VSB - TU Ostrava, Czech Republic, June 4 - 6, 2015.
- 3) Stefano Ubaldini, Jana Kadukova, Pietro Fornari, Daniela Guglietta, Alena Luptakova, Bio-hydrometallurgical circuit for treatment of exhaust alkaline batteries, proceedings of “The 18<sup>th</sup> International Conference of Waste Recycling”, Miskolc, Hungary, ISBN: 978-615-5216-61-9 (9 pgs total), October 9-10, 2014.
- 4) Renata Marcincakova, Jana Kadukova, Anna Mrazikova, Oksana Velgosova, Alena Luptakova, Stefano Ubaldini, Metal bioleaching from spent lithium-ion batteries using acidophilic bacterial strains, proceedings of the 3<sup>rd</sup> International Scientific Conference on Biotechnologies and Metals, Edited by Kadukova Jana, Luptakova Alena, Velgosova Oksana, ISBN: 978-80-553-1787-8, pp. 45-46, Kosice, Slovak Republic, September 17 – 19, 2014.
- 5) S. Ubaldini, A. Luptakova, J. Jencarova, P. Fornari, P. Pizzichemi, Development of bio-hydrometallurgical processes for the valorization of spent batteries, Proceedings of the XVII International Conference on Waste Recycling, Kosice, Slovakia, ISBN: 978-80-970034-6-3, pp.79-82, November 21<sup>st</sup> –22<sup>nd</sup>, 2013.
- 6) Ubaldini S., Luptakova A., Macingova E., Fornari P., Pizzichemi P., Innovative Biohydrometallurgical Processes for Decontamination of Acid Mine Drainage, Proceedings of the 13<sup>th</sup> International Conference on Environmental Science and Technology (CEST 2013), Editor T.D. Lekkas, paper ID: CEST2013\_0275, ISBN: 978-960-7475-51-0, ISSN: 1106-5516, 5-7 September 2013, Athens, Greece (total pages n. 8).
- 7) S. Ubaldini, A. Luptakova, P. Fornari and E. Yoplac, Application of Innovative Remediation Processes to Mining Effluents contaminated by Heavy Metals, published in E3S Web of Conferences 1, by EDP Sciences, doi:10.1051/e3sconf/20130125001, Volume 1, art. N. 25001, pp. 1-4, 2013.

### **Altre pubblicazioni:**

- 1) S. Ubaldini, A. Luptakova, M. Prascakova, E. Macingova, J. Jencarova, Possibilities of bio-hydrometallurgical treatment of spent alkaline batteries, Book of Abstracts of the 5<sup>th</sup> International Conference Applied Natural Sciences 2015, 30<sup>th</sup> September – 2<sup>nd</sup> October 2015, Jasná, Low Tatras, Slovak Republic, in corso di stampa 2015 (riassunto).
- 2) S. Ubaldini, J. Kadukova, A. Mrazikova, P. Fornari, A. Luptakova, R. Marcincakova, P. Pizzichemi, Application of innovative processes for the valorization of alkaline spent batteries, 17th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction PRES 2014, 23-27 August 2014 Prague, Czech Republic (riassunto).
- 3) Stefano Ubaldini, Jana Kadukova, Pietro Fornari, Daniela Guglietta, Alena Luptakova, Bio-hydrometallurgical circuit for treatment of exhaust alkaline batteries, Book of Abstracts of “The 18<sup>th</sup> International Conference of Waste Recycling”, ISBN: 978-615-5216-60-2, pg. 27, Miskolc, Hungary, October 9-10, 2014 (riassunto).
- 4) Ubaldini S., Luptakova A., Macingova E., Fornari P., Pizzichemi P., Innovative Biohydrometallurgical Processes for Decontamination of Acid Mine Drainage, Volume of abstracts of the 13<sup>th</sup> International Conference on Environmental Science and Technology (CEST 2013), pg 128, Editor T.D. Lekkas, paper ID: CEST2013\_0275, ISBN: 978-960-7475-51-0, ISSN: 1106-5516, 5-7 September 2013, Athens, Greece (riassunto).
- 5) S. Ubaldini, A. Luptakova, J. Jencarova, P. Fornari, P. Pizzichemi, Development of bio-hydrometallurgical processes for the valorization of spent batteries, Book of Abstracts of the XVII International Conference on Waste Recycling, Kosice, Slovakia, p. 6, November 21<sup>st</sup> –22<sup>nd</sup>, 2013 (riassunto).

### **Banche dati:**

- 1) Banca dati su campioni di pile esaurite caratterizzate, selezionati sul territorio della Repubblica Slovacca.
- 2) Banca dati su campioni di pile esaurite caratterizzate, selezionati sul territorio Italiano.

### **Nuovi processi:**

- 1) Processo biologico, con uso di microorganismi, per il recupero di metalli dalle pile esaurite.
- 2) Processo elettrochimico adatto alla rimozione e purificazione di metalli pesanti da pile esaurite.
- 3) Rimozione metallica selettiva mediante bioprecipitazione da soluzioni, dopo lisciviazione/biolisciviazione di pile esaurite.

### **Trasferimento innovazioni:**

- 1) Imprese operanti nel settore ambientale in Italia (FINMECCANICA GLOBAL SERVICES, Roma, Italia; E-GEOS SPA, Matera, Italia; SODAI Italia s.p.a., ECOMETAL s.r.l., IRISAT S.r.l. Ingegneria per le Risorse ambientali e del territorio, Anzio, Italia), Repubblica Ceca (CEKOMETAL), Repubblica Slovacca (ENVIRONCENTRUM SRO, Kosice, Slovacchia), Belgio (INTERNATIONAL BUREAU FOR ENVIRONMENTAL STUDIES - IBES, Bruxelles, Belgio), Romania (CMC Chimie Srl, Baia Mare, Romania).
- 2) Trasferimento di conoscenze di task, specifiche della ricerca applicata e della ricerca di base, orientate verso la cooperazione internazionale (Department Ecole Nationale Supérieure des Mines de Saint-Etienne, ASSOCIATION POUR LA RECHERCHE ET LE DEVELOPPEMENT DES METHODES ET PROCESS, Parigi, Francia; Association pour la Recherche et le Développement des Méthodes et Processus Industriels (ARMINES), Parigi, Francia).
- 3) Applicazione di nuove conoscenze all'interno di materiali educativi di università ed istituzioni di ricerca:

UNIVERSITY OF MISKOLC, Ungheria, Department of Raw Materials Preparation and Environmental Processing;

Department of Non-ferrous Metals and Waste Treatment, Faculty of Metallurgy, Technical University of Kosice, Repubblica Slovacca;

Department of Material Science, Faculty of Metallurgy, Technical University of Kosice, Slovak Republic;

Dipartimento di Chimica, Ingegneria Chimica e Materiali dell'Università dell'Aquila;

TECHNICAL UNIVERSITY OF CRETE, School Mineral Resources Eng., Chania, Grecia.

**Laboratori congiunti:**

- 1) Laboratorio di elettrochimica (sezione di idrometallurgia) presso IGAG-CNR.
- 2) Laboratorio di metallurgia of Technical University in Kosice, Faculty of Metallurgy, Department of material science, Košice, Slovak Republic.
- 3) Laboratorio di Bio-Idrometallurgia of Department of Mineral Biotechnologies of the Institute of Geotechnics of Slovak Academy of Sciences, Kosice, Repubblica Slovacca.
- 4) Laboratorio of biometallurgia e biotecnologie ambientali, Faculty of Metallurgy, Technical University of Kosice, Slovak Republic.

**Altro:**

- 1) Organizzazione di seminario c/o IGAG-CNR nei giorni dal 24 al 30 Settembre 2015, sul tema: "Using of microscopy methods for morphology study of biodeteriorated surface", tenuto dal Dr. Miloslav Luptak, Techical University in Kosice, Faculty of Metallurgy, Kosice – Slovak Republic.
- 2) Organizzazione di seminario c/o IGAG-CNR nei giorni dal 02 al 08 Ottobre 2014, sul tema: "Non Conventional technological Processes and the measuring of the selected materials physical properties", tenuto dal Dr. Miloslav Luptak, Techical University in Kosice, Faculty of Metallurgy, Kosice – Slovak Republic.
- 3) Organizzazione di seminario c/o IGAG-CNR nel giorno 07 Ottobre 2014, da parte di:  
Dr. Alena Luptakova (Institute of Geotechnics, Slovak Academy of Sciences – IG SAS), title: Biohydrometallurgical research in the frame work of cooperation between Slovak Academy of Sciences and IGAG – CNR;  
Dr. Eva Macingova (IG SAS), title: Environmental analysis on the Department of Mineral Biotechnology of IG SAS;
- Mgr. Ingrida Kotulicova (IG SAS), title: Zoobentos as bioindicator of water quality;
- Dr. Miloslav Luptak (Faculty of Metallurgy, Technical University of Kosice), title: Non-Conventional technological Processes.
- 4) S.Ubaldini. Development of innovative processes for the valorization of spent batteries, attività scientifiche svolte nel 2014 nell'ambito dell'accordo di cooperazione tra il CNR e il SAV – Accademia delle Scienze Slovacca, anni 2013-2015, Progetto CNR n. 1. Rapporto Annuale 2014.
- 5) S.Ubaldini. Development of innovative processes for the valorization of spent batteries, accordo di cooperazione scientifica tra il CNR e il SAV – Accademia delle Scienze Slovacca, anni 2013-2015, Progetto CNR n. 1. Relazione Tecnica 2014.
- 6) S.Ubaldini. Development of innovative processes for the valorization of spent batteries, attività scientifiche svolte nel 2013 nell'ambito dell'accordo di cooperazione tra il CNR e il SAV – Accademia delle Scienze Slovacca, anni 2013-2015, Progetto CNR n. 1. Rapporto Annuale 2013.
- 7) S.Ubaldini. Development of innovative processes for the valorization of spent batteries, accordo di cooperazione scientifica tra il CNR e il SAV – Accademia delle Scienze Slovacca, anni 2013-2015, Progetto CNR n. 1. Relazione Tecnica 2013.
- 8) Organizzazione di seminario c/o IGAG-CNR nei giorni dal 16 al 22 Settembre 2013, sul tema: "The study of magnetic properties of biogenic iron sulphides", tenuto dal Dr. Miloslav Luptak, Techical University in Kosice, Faculty of Metallurgy, Kosice - Slovak Republic.
- 9) A. Luptakova è stata supervisore/consulente - nell'ambito della tesi di dottorato (PhD) - della studentessa Anna Mrazikova (Department of Material Science, Faculty of Metallurgy, Technical University of Kosice, Slovak Republic). Titolo della tesi di PhD: Bioleaching of metals from electronic wastes.
- 10) A. Luptakova è stata supervisore/consulente - nell'ambito della tesi di dottorato (PhD) - della studentessa Renata Marcincakova (Department of Material Science, Faculty of Metallurgy, Technical University of Kosice, Slovak Republic). Titolo della tesi di PhD: Obtaining lithium from spent batteries by biometallurgy.

## **7. Detailed information on results indicated under point 6**

### ***Scientific publications on international reviews with IF :***

- 1) S. Ubaldini, J. Kadukova, A. Mrazikova, P. Fornari, A. Luptakova, R. Marcincakova, P. Pizzichemi. Application of innovative processes for the valorization of alkaline spent batteries, Chemical Engineering Transactions, ISBN 978-88-95608-30-3; ISSN 2283-9216, Vol. 39, pp. 1609-1614, 2014. DOI: 10.3303/CET1439269.
- 2) Eva Mačingová, Stefano Ubaldini, Alena Luptáková. Study of manganese removal in the process of mine water remediation, Journal of the Polish Mineral Engineering Society, ISSN 1640-4920, in press 2015.
- 3) R. Marcincakova, J. Kadukova, A. Mrazikova, O. Velgosova, A. Luptakova, S. Ubaldini. Metal bioleaching from spent lithium-ion batteries using acidophilic bacterial strains, Journal of the Polish Mineral Engineering Society, ISSN 1640-4920, in press 2015.

### ***Publications in international congress proceedings:***

- 1) Stefano Ubaldini, Alena Luptakova, Maria Prascakova, Eva Macingova, Jana Jencarova, Possibilities of Bio-hydrometallurgical treatment of spent alkaline batteries, Proceedings of the 5th International Conference “Applied Natural Sciences 2015“, Jasná, Low Tatras, Slovak Republic, September 30 - October 2, in press 2015.
- 2) Eva Mačingová, Stefano Ubaldini, Alena Luptáková. Study of manganese removal in the process of mine water remediation, Proceedings of the 19<sup>th</sup> Conference on Environment and Mineral Processing – Part I, ISBN 978-80-248-3753-6, pp. 61-66, Edited by VSB - TU Ostrava, Czech Republic, June 4 - 6, 2015.
- 3) Stefano Ubaldini, Jana Kadukova, Pietro Fornari, Daniela Guglietta, Alena Luptakova, Bio-hydrometallurgical circuit for treatment of exhaust alkaline batteries, proceedings of “The 18<sup>th</sup> International Conference of Waste Recycling”, Miskolc, Hungary, ISBN: 978-615-5216-61-9 (9 pgs total), October 9-10, 2014.
- 4) Renata Marcincakova, Jana Kadukova, Anna Mrazikova, Oksana Velgosova, Alena Luptakova, Stefano Ubaldini, Metal bioleaching from spent lithium-ion batteries using acidophilic bacterial strains, proceedings of the 3<sup>rd</sup> International Scientific Conference on Biotechnologies and Metals, Edited by Kadukova Jana, Luptakova Alena, Velgosova Oksana, ISBN: 978-80-553-1787-8, pp. 45-46, Kosice, Slovak Republic, September 17 – 19, 2014.
- 5) S. Ubaldini, A. Luptakova, J. Jencarova, P. Fornari, P. Pizzichemi, Development of bio-hydrometallurgical processes for the valorization of spent batteries, Proceedings of the XVII International Conference on Waste Recycling, Kosice, Slovakia, ISBN: 978-80-970034-6-3, pp.79-82, November 21<sup>st</sup> –22<sup>nd</sup>, 2013.
- 6) Ubaldini S., Luptakova A., Macingova E., Fornari P., Pizzichemi P., Innovative Biohydrometallurgical Processes for Decontamination of Acid Mine Drainage, Proceedings of the 13<sup>th</sup> International Conference on Environmental Science and Technology (CEST 2013), Editor T.D. Lekkas, paper ID: CEST2013\_0275, ISBN: 978-960-7475-51-0, ISSN: 1106-5516, 5-7 September 2013, Athens, Greece (total pages n. 8).
- 7) S. Ubaldini, A. Luptakova, P. Fornari and E. Yoplac, Application of Innovative Remediation Processes to Mining Effluents contaminated by Heavy Metals, published in E3S Web of Conferences 1, by EDP Sciences, doi:10.1051/e3sconf/20130125001, Volume 1, art. N. 25001, pp. 1-4, 2013.

***Other publications:***

- 1) S. Ubaldini, A. Luptakova, M. Prascakova, E. Macingova, J. Jencarova, Possibilities of bio-hydrometallurgical treatment of spent alkaline batteries, Book of Abstracts of the 5<sup>th</sup> International Conference Applied Natural Sciences 2015, 30<sup>th</sup> September – 2<sup>nd</sup> October 2015, Jasná, Low Tatras, Slovak Republic, in press 2015 (abstract).
- 2) S. Ubaldini, J. Kadukova, A. Mrazikova, P. Fornari, A. Luptakova, R. Marcincakova, P. Pizzichemi, Application of innovative processes for the valorization of alkaline spent batteries, 17th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction PRES 2014, 23-27 August 2014 Prague, Czech Republic ((abstract).
- 3) Stefano Ubaldini, Jana Kadukova, Pietro Fornari, Daniela Guglietta, Alena Luptakova, Bio-hydrometallurgical circuit for treatment of exhaust alkaline batteries, Book of Abstracts of “The 18<sup>th</sup> International Conference of Waste Recycling”, ISBN: 978-615-5216-60-2, pg. 27, Miskolc, Hungary, October 9-10, 2014 (abstract).
- 4) Ubaldini S., Luptakova A., Macingova E., Fornari P., Pizzichemi P., Innovative Biohydrometallurgical Processes for Decontamination of Acid Mine Drainage, Volume of abstracts of the 13<sup>th</sup> International Conference on Environmental Science and Technology (CEST 2013), pg 128, Editor T.D. Lekkas, paper ID: CEST2013\_0275, ISBN: 978-960-7475-51-0, ISSN: 1106-5516, 5-7 September 2013, Athens, Greece (abstract).
- 5) S. Ubaldini, A. Luptakova, J. Jencarova, P. Fornari, P. Pizzichemi, Development of bio-hydrometallurgical processes for the valorization of spent batteries, Book of Abstracts of the XVII International Conference on Waste Recycling, Kosice, Slovakia, p. 6, November 21<sup>st</sup> –22<sup>nd</sup>, 2013 (abstract).

***Data bases:***

- 1) Data base on samples of spent batteries characterized, selected on the territory of the Slovak Republic .
- 2) Data base on samples of spent batteries characterized, selected on the Italian territory.

***New processes :***

- 1) Biological process, with use of chemoautotrophic bacteria, for the recovery of metals from used batteries .
- 2 ) Electrochemical process suitable for removal and purification of heavy metals from exhausted batteries.
- 3) Selective removal of metals by bioprecipitation from solutions after leaching/bioleaching exhausted batteries.

***Knowledge transfer:***

- 1) Companies operating in the environmental sector in Italy (FINMECCANICA GLOBAL SERVICES, Roma, Italy; E-GEOS SPA, Matera, Italy; SODAI Italia s.p.a., ECOMETAL s.r.l., IRISAT S.r.l. Ingegneria per le Risorse ambientali e del territorio, Anzio, Italy), Czech Republic (CEKOMETAL), Slovak Republic (ENVIRONCENTRUM SRO, Kosice, Slovakia), Belgium (INTERNATIONAL BUREAU FOR ENVIRONMENTAL STUDIES - IBES, Bruxelles, Belgium), Romania (CMC Chimie Srl, Baia Mare, Romania).
- 2) Transfer of knowledge to consequent task within specific oriented applied research and basic research within internationally oriented cooperation (Department Ecole Nationale Supérieure des Mines de Saint-Etienne, ASSOCIATION POUR LA RECHERCHE ET LE DEVELOPPEMENT DES METHODES ET PROCESS, Parigi, Francia; Association pour la Recherche et le Développement des Méthodes et Processus Industriels (ARMINES), Parigi, Francia).
- 3) Application of new knowledge into educative materials of universities and research institutions: UNIVERSITY OF MISKOLC, Hungary, Department of Raw Materials Preparation and Environmental Processing;  
Department of Non-ferrous Metals and Waste Treatment, Faculty of Metallurgy, Technical University of Kosice, Repubblica Slovacca;  
Department of Material Science, Faculty of Metallurgy, Technical University of Kosice, Slovak Republic;  
Dipartimento di Chimica, Ingegneria Chimica e Materiali dell’Università dell’Aquila;  
TECHNICAL UNIVERSITY OF CRETE, School Mineral Resources Eng., Chania, Greece.

***Joint laboratories:***

- 1) Electrochemical Laboratory (Hydrometallurgy section) of IGAG-CNR.
- 2) Laboratory of metallurgy of Technical University in Kosice, Faculty of Metallurgy, Department of material science, Košice, Slovak Republic.
- 3) Bio-Hydrometallurgy Laboratory of Department of Mineral Biotechnologies of Institute of Geotechnics-SAV, Kosice, Slovak Republic.
- 4) Laboratory of biometallurgy and environmental biotechnology, Faculty of Metallurgy, Technical University of Kosice, Slovak Republic.

***Other:***

- 1) Organizing of the seminar held at IGAG-CNR on days 24 to 30 September 2015, on the theme: "Using of microscopy methods for morphology study of biodeteriorated surface", held by Dr. Miloslav Luptak, Technical University in Kosice, Faculty of Metallurgy, Kosice – Slovak Republic.
- 2) Organizing of the seminar held at IGAG-CNR on days 2 to 08 October 2014, on the theme: "Non Conventional technological Processes and the measuring of the selected materials physical properties", held by Dr. Miloslav Luptak, Technical University in Kosice, Faculty of Metallurgy, Kosice – Slovak Republic.
- 3) Organizing of the seminar held at IGAG-CNR on 7 October 2014, by Dr. Alena Luptakova (Institute of Geotechnics, Slovak Academy of Sciences – IG SAS), title: Biohydrometallurgical research in the frame work of cooperation between Slovak Academy of Sciences and IGAG – CNR; Dr. Eva Macingova (IG SAS), title: Environmental analysis on the Department of Mineral Biotechnology of IG SAS;
- Mgr. Ingrida Kotulicova (IG SAS), title: Zoobentos as bioindicator of water quality;
- Dr. Miloslav Luptak (Faculty of Metallurgy, Technical University of Kosice), title: Non-Conventional technological Processes.
- 4) S.Ubaldini. Development of innovative processes for the valorization of spent batteries, scientific activities carried out during the year 2014 in the frame of the cooperation agreement between CNR and SAV – Slovak Academy of the Sciences, years 2013-2015, Project CNR n. 1. Annual Report 2014.
- 5) S.Ubaldini. Development of innovative processes for the valorization of spent batteries, scientific cooperation agreement between CNR and SAV – Slovak Academy of the Sciences, years 2013-2015, Project CNR n. 1. Technical Report 2014.
- 6) S.Ubaldini. Development of innovative processes for the valorization of spent batteries, scientific activities carried out during the year 2014 in the frame of the cooperation agreement between CNR and SAV – Slovak Academy of the Sciences, years 2013-2015, Project CNR n. 1. Annual Report 2013.
- 7) S.Ubaldini. Development of innovative processes for the valorization of spent batteries, scientific cooperation agreement between CNR and SAV – Slovak Academy of the Sciences, years 2013-2015, Project CNR n. 1. Technical Report 2013.
- 8) Organizing of the seminar held at IGAG - CNR on days 16 to 22 September 2013 on the theme: "The study of magnetic properties of biogenic iron sulphides", by Dr. Miloslav Luptak, Technical University in Kosice, Faculty of Metallurgy, Kosice – Slovak Republic.
- 9) A. Luptakova was the supervisor/consultant in the framework of PhD study of student Anna Mrazikova (Department of Material Science, Faculty of Metallurgy, Technical University of Kosice, Slovak Republic). Title of PhD-theses: Bioleaching of metals from electronic wastes.
- 10) A. Luptakova was the supervisor/consultant in the framework of PhD study of student Renata Marcincakova (Department of Material Science, Faculty of Metallurgy, Technical University of Kosice, Slovak Republic). Title of PhD-theses: Obtaining lithium from spent batteries by biometallurgy.

## **8. Formazione di giovani ricercatori**

Nel corso dei tre anni del progetto è stata realizzata la formazione di giovani ricercatori e studenti post-laurea articolata in: acquisizione di nuove metodologie di analisi, applicazione del piano fattoriale degli esperimenti e trasferimento di nuove tecnologie flessibili, con lo scopo di sviluppare processi fisico-chimici e biologico-chimici innovativi e sostenibili, per la valorizzazione di pile esaurite.

## **8. Training of young researchers**

During the three years of the project was carried out the training of young researchers and post-graduate students articulated into acquisition of new methods of analysis, implementation of the factorial plan of experiments and transfer of new technologies, flexible, in order to develop innovative and sustainable physicochemical and biological-chemical processes, to valorise the spent batteries.

## **9. Motivazione degli sviluppi della collaborazione negli anni successivi**

**La collaborazione, ha contribuito a rafforzare le relazioni scientifiche e tecnologiche tra le strutture di ricerca dei due Paesi, ed a coinvolgere nelle tematiche oggetto degli studi altre istituzioni di ricerca europee - sia pubbliche che private - anche in relazione all'impegno comune volto alla presentazione di proposte di finanziamento alla Commissione Europea nell'ambito del Programma Quadro Horizon 2020, nell'ambito del quale sono state presentate le seguenti proposte (con IGAG quale coordinatore delle stesse) nel settore delle materie prime:**

- 1) "Sustainable Mining And Recovery Technologies for Critical Raw Materials in Europe" (SMART-rawmaterials), Call: H2020-SC5-2014-one-stage, Topic: SC5-11a-2014;
- 2) "The Innovative, Zero-waste Production of Phosphoric Acid using Hydrochloric Acid and the Valorisation of Phosphogypsum Wastes" (Phospho-Chlor) Call: H2020-SC5-2015-one-stage, Topic: SC5-11e-2015.

E' in corso di elaborazione una proposta Life, avente per oggetto la valorizzazione delle materie prime seconde, attraverso processi innovativi e sostenibili sotto l'aspetto ambientale ed economico, che verrà presentata nell'ambito della prossima call 2015.

La proficua cooperazione scientifica tra IGAG-CNR ed Institute of Geotechnics of the Slovak Academy of Sciences ha consentito di ottenere - nel corso del presente Progetto - gli importanti prodotti elencati al punto 7, in linea con gli obiettivi prefissati.

**Di conseguenza, le numerose imprese che sono state coinvolte nella finalizzazione del trasferimento dell'innovazione tecnologica, sono interessate ad un'approfondimento degli studi con relativo sviluppo ed ottimizzazione dei parametri del processo su impianto pilota, al fine di realizzare l'impianto industriale.**

Pertanto, in relazione a tale forte interesse ed al beneficio per l'ambiente che può derivare dalla realizzazione del processo proposto, ci si auspica di poter continuare la collaborazione; si è pertanto deciso di preparare e presentare un nuovo progetto CNR-SAV, intitolato "Sviluppo di processi innovativi per la valorizzazione di pile esaurite", relativo al prossimo biennio 2016-2017.

## **9. Reasons for cooperative project developments in the following years**

The collaboration has helped to strengthen the scientific and technological relations between the research structures of the two Countries, and to engage, in the themes discussed in the studies, other European research institutions - both public and private - also in connection with the shared commitment to the presentation of financing proposals to the European Commission under the framework Programme Horizon 2020, in which were presented the following proposals (with IGAG as coordinator thereof) in the field of raw materials:

- 1) "Sustainable Mining And Recovery Technologies for Critical Raw Materials in Europe" (SMART-rawmaterials), Call: H2020-SC5-2014-one-stage, Topic: SC5-11a-2014;
- 2) "The Innovative, Zero-waste Production of Phosphoric Acid using Hydrochloric Acid and the Valorisation of Phosphogypsum Wastes" (Phospho-Chlor) Call: H2020-SC5-2015-one-stage, Topic: SC5-11e-2015.

It has been prepared, under draft, a Life proposal, which relates to the enhancement of secondary raw materials, through innovative processes and sustainable from the environmental and economic, that will be presented at the next call in 2015.

The fruitful cooperation between scientific and IGAG-CNR Institute of Geotechnics of the Slovak Academy of Sciences has allowed to obtain - in the course of this project - the relevant products listed above, in line with its objectives.

**As a direct consequence, many companies that have been involved in the finalization of the transfer of technological innovation, are interested in an in-depth study with its development and optimization of process parameters on the pilot plant in order to realize the industrial plant.**

Therefore, in connection with such strong interest and the benefit to the environment that may arise from the implementation of the proposed process, it is hoped to continue the collaboration; it was decided to prepare and submit a new draft CNR-SAV, entitled "Development of innovative processes for the exploitation of dead batteries", which covers the next two years from 2016 to 2017.

M. Ubaldini

(firma del responsabile italiano del progetto)  
Dr. Stefano Ubaldini

P. Messina

(firma del direttore)  
Dr. Paolo Messina

A. Luptakova

(signature of the Slovak project leader)  
Ing. Alena Luptakova, PhD  
(anche fax)

