



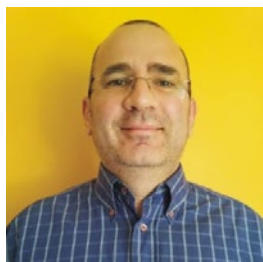
START

NEWSLETTER

RECOVER-REFORM-REUSE

for a Sustainable Future

EDITORIAL



Dear members of the START community,

Welcome to the second issue of the START project Newsletter! In this issue, we will share with you some highlights from our recent events and activities, and you will learn more about START with STARTY, our friendly robot that helps us explain the project scope. We

will also introduce you to the members of our Scientific Advisory Board (SAB), who provide us with valuable guidance and feedback on our work. They are:

- Doug Crane: Chief Technology Officer (CTO) of DTP Thermoelectrics and former Director of Thermoelectric Engineering at Alphabet Energy, Inc.
- Jean-Yves Escabasse: Chemical Engineer and Doctor with 40 years of experience in R&D and innovation within several materials industry sectors.
- Julie Hollis: Secretary General of EuroGeoSurveys (EGS) – The Geological Surveys of Europe.

We are very grateful for their support and welcome them on this journey! In this issue, we have an exclusive interview with Julie Hollis, where she presents the mission and objectives of the EuroGeoSurveys (EGS) and the contribution to the EU priorities related with the Green Deal and the EU Action Plan on Critical Raw Materials (CRM). She also shares her views on the EU's resilience towards CRM security and the possible synergies between EGS and START.

In addition, we have two technical pills for you: one related to the geology of tetrahedrites (the main mineral used in START) and another describing the use of powder technology for processing tetrahedrites into high-performance thermoelectric materials. Finally, we will take you on a tour around two of our consortium partners: TEGnology (from Denmark) and RGS Development (from the Netherlands), both small enterprises that develop innovative thermoelectric solutions for different sectors.

We hope you enjoy reading this Newsletter and we invite you to stay tuned for more updates from START on our website and social media channels.

(F. Neves)

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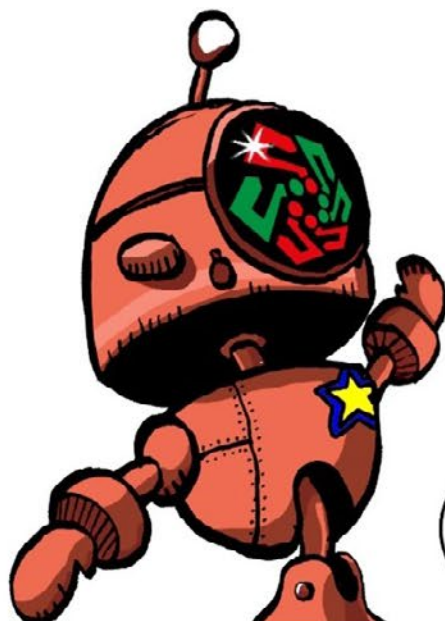
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STARTY – 2: THE GEOLOGY WORK IN START

2 GEOLOGY



2050

EUROPE HAS THE INTENTION OF BECOMING THE WORLD'S FIRST CLIMATE-NEUTRAL CONTINENT BY 2050, WHICH MEANS IMPLEMENTING THE 'EUROPEAN GREEN DEAL'.



TO ACHIEVE THIS (GREEN) ENERGY TRANSITION, MINERAL RESOURCES ARE CRUCIAL, MOSTLY DRIVEN BY DEMAND IN DEVELOPING COUNTRIES AND BY GREEN ENERGY TECHNOLOGIES.



ACCESS TO SUSTAINABLE RESOURCES IS A KEY FOR STRENGTHENING THE EUROPEAN RESILIENCE IN RELATION TO RAW MATERIALS AND ACHIEVING THE NEEDED RESOURCES' SECURITY REQUIRES SEVERAL ACTIONS.



2050
CLIMATE
NEUTRALITY
SUSTAINABLE
RESOURCES
SECURITY
ACTION
DESIGN
TECHNOLOGIES
EUROPE
GREEN
ACTION
CIRCULAR
ECONOMY
REDUCE
WORLD
RENEWABLE
ZERO
EMISSIONS
FOOTPRINT
PEOPLE
RESPONSIBLE
STANDARDS
ATMOSPHERE
CARBON
FUTURE
VEHICLES
ENERGY
NEW
REUSE
MATERIALS
SCARCITY
RAW
MANKIND
DESIGN
ACTION
SECURITY

ENERGY STORAGE

SOLAR PANELS

MAGNETS

WIND TURBINES

ELECTRIC MOTORS

WIRING

POWER GRIDS

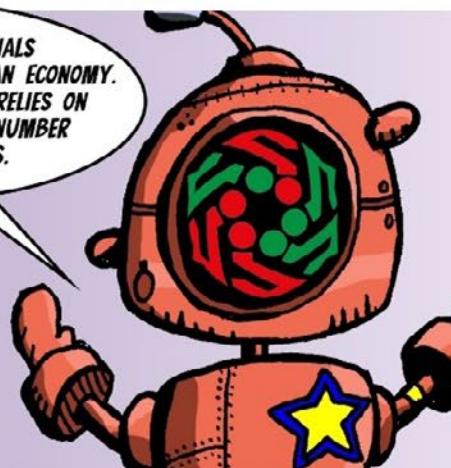
HARDWARE

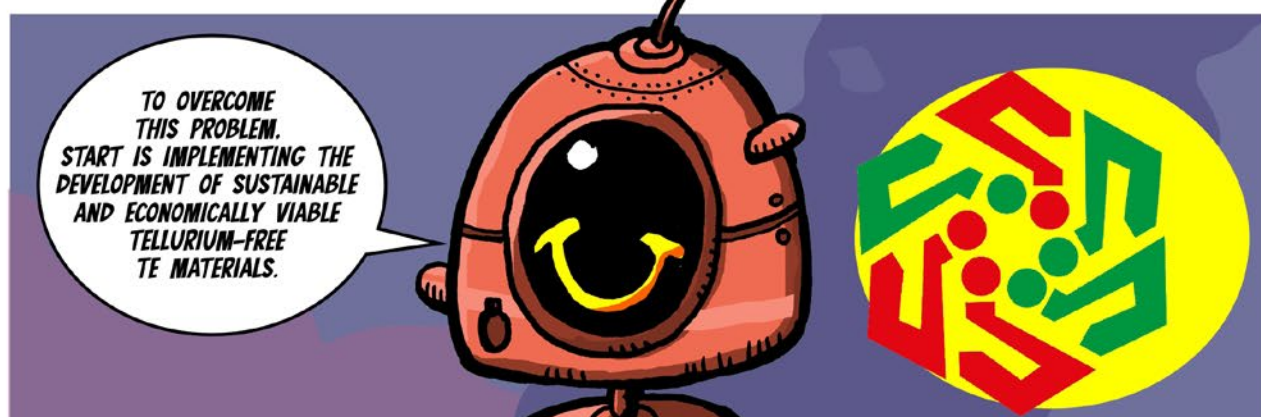
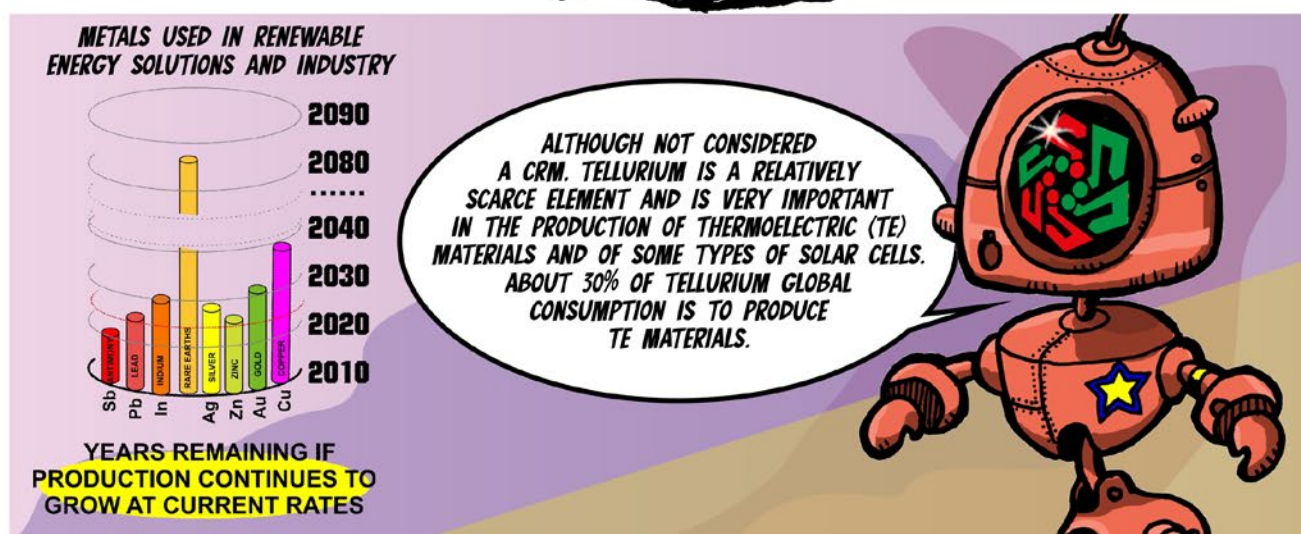
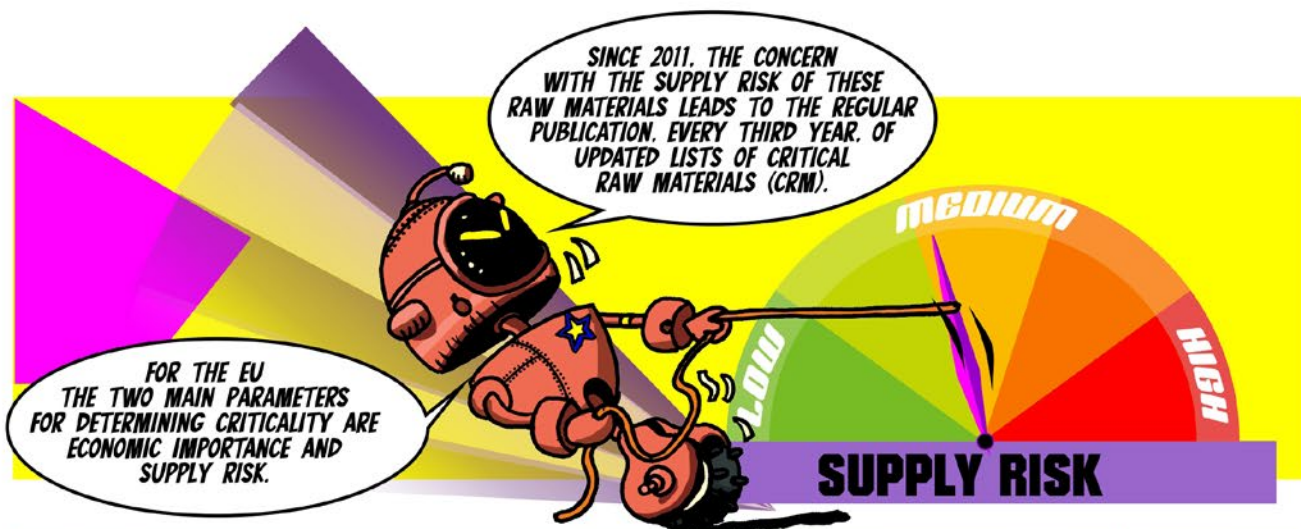
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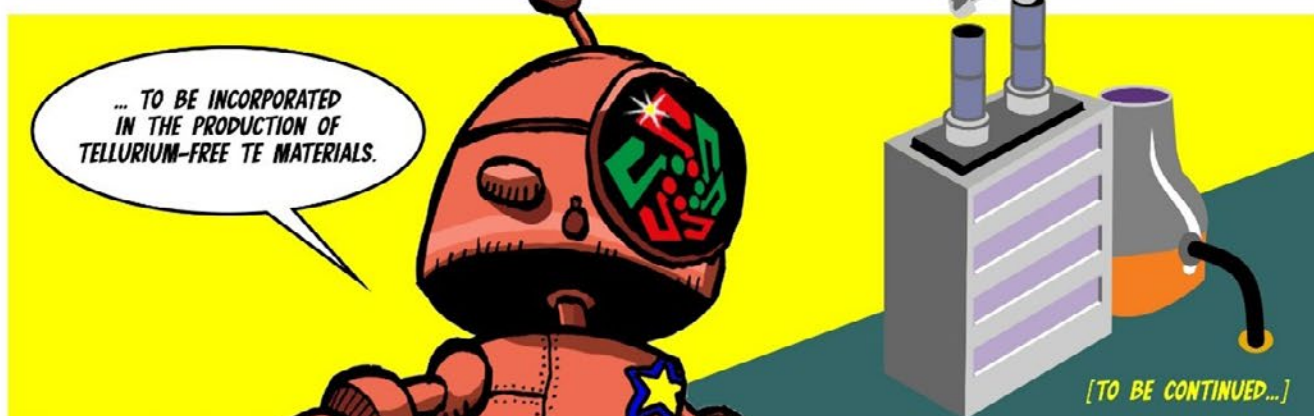
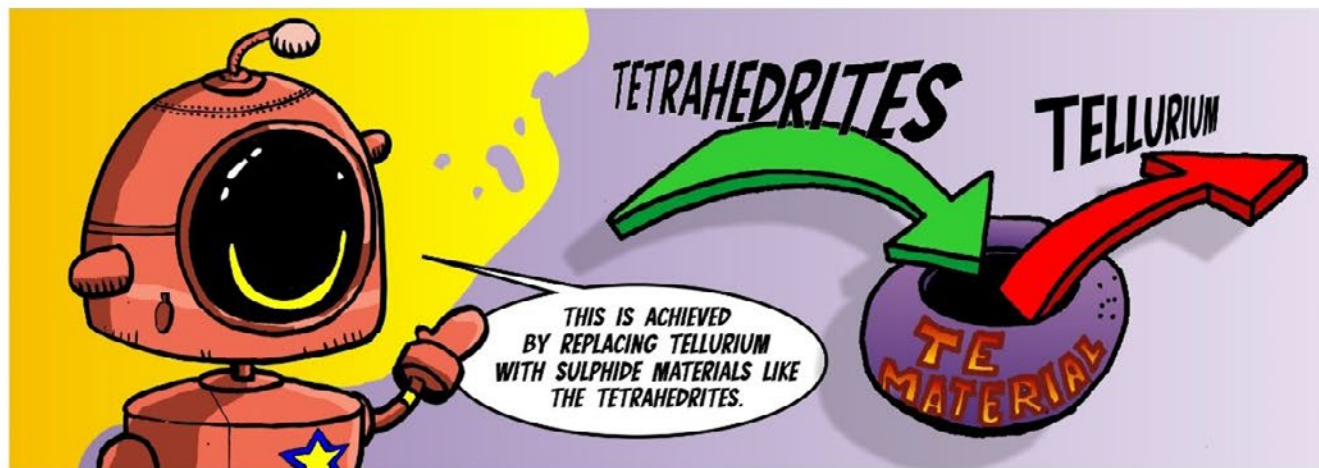
BATTERIES

RAW MATERIALS

MINERAL RAW MATERIALS ARE CRUCIAL TO THE EUROPEAN ECONOMY. TECHNOLOGICAL PROGRESS RELIES ON ACCESS TO A GROWING NUMBER OF RAW MATERIALS.







START CHRONICLES: GEOLOGY AND MORE

NEWS FROM WORK PACKAGE 2 “SELECTION OF MINE WASTE SITES; PHYSICAL MINERALS SEPARATION AND CONCENTRATION”: TETRAHEDRITES COLLECTED IN SLOVAKIA HAVE BEEN ANALYSED AND SUCCESSFULLY CONCENTRATED

One of the countries where START is looking for tetrahedrites in mining sites is Slovakia. The partner Štátny Geologický ústav Dionýza Štúra (State Geological Institute of Dionýz Štúr, SGUDS), one of the partners working in START's Work Package 2, has reviewed the Strieborná vein deposit in Rožňava and analysed the samples collected there (Figure 1), and finally attempted to separate the tetrahedrite with a few different methods.

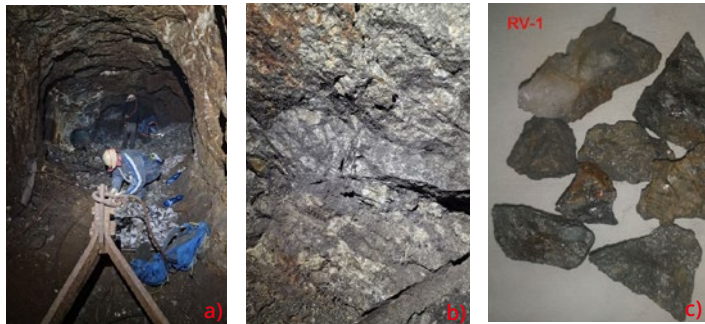


Figure 1 - (a) Strieborná mine, (b) mineral vein (c) raw sample after the homogenization and quartering (after the first crushing degree).

The Strieborná vein deposit of the Rožňava ore field (ROF) is situated at the south-eastern margin of the Western Carpathian basement units, inside the Gelnica Group formation of the Gemeric Superunit. The Early Paleozoic Gelnica Group forms the oldest sequence of the metasedimentary/metavolcanitic formations of the Gemeric Superunit. The ROF area is penetrated by the subparallelly arranged hydrothermal siderite– sulphidic veins of SE–NW direction. The history of mining in the ROF started in the 13th century, when the greatest interest was focused mainly on gold, silver, copper, antimony and mercury. In 1981, northwards from the Rožňava mining city, a new Strieborná vein was discovered, and it became the most significant vein structure in the ROF. The vein position was compared with the historically known, parallelly oriented Mária vein. The distance between the Strieborná and Mária veins is 600 m (Figure 2). The vein filling and the structural position in the ore field suggest a close link between the veins origin and structural evolution. The Strieborná vein genesis is the product of multiple epigenetic hydrothermal mineralizations, with a close relationship between the vein filling and rheologically contrasting environment. Consequently, the vein does not crop out on the surface. The largest accumulation is known from the 10th mine horizon (20 m b.s.l.) in the total length of 1300 m. The continuation of the vein gradually decays in the overlaying darkblack metapelites and grey metasandstones.

Metaclasts often contain layers of quartz and lithic wackes. Below the 10th level (below 0 m a.s.l.) the ore body is situated within metasediments and metavolcanic rocks¹.

Major vein minerals are medium to the coarse-grained siderite of two generations and younger multi-generational quartz–sulphide mineralization of two generations. The most abundant ore minerals are tetrahedrite, chalcopyrite, pyrite and arsenopyrite. Brittle, steel-grey coloured

tetrahedrite, which is the most important ore mineral, is spatially controlled by the older siderite that is in the form of reticulated veins and clusters. A more brittle tetrahedrite variety with steel blue colour and high metallic lustre is usually enriched by Cu, Ag, Bi, Sb and Hg. A darker low lustre variety contains more Zn and Fe. The high content of silver in tetrahedrite was the reason for the name of the Strieborná vein. The concentration of tetrahedrite in the vein bodies has a zonal distribution, and gradually decreases downwards to underlying rocks where it is substituted by pyrite. Quartz is the main gangue mineral and forms several generations. The products of the youngest quartz– sulphide phase are tetrahedrite, kobellite, bismuthinite, bournonite, jamesonite and stibnite.

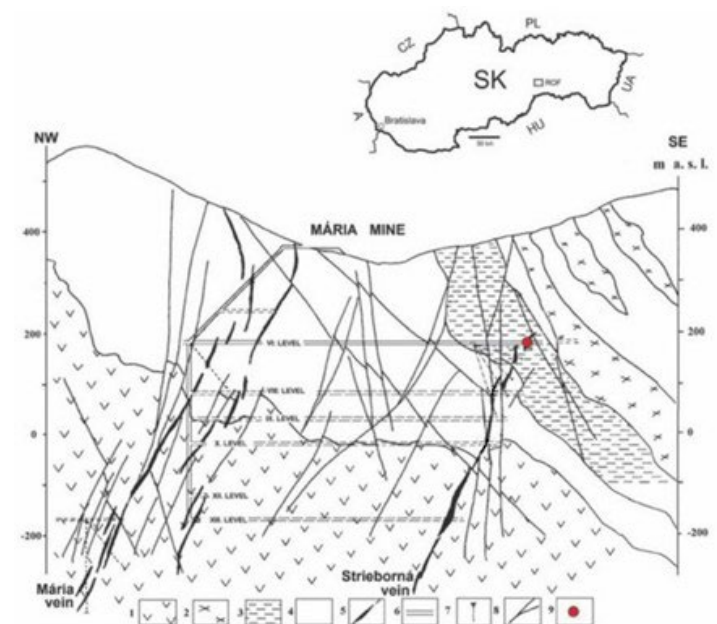


Figure 2 - Geological cross-section through the NE part of Rožňava-Mária ore segment (Mesarčík et al., 1991— modified).

- 1 — recrystallized metavolcanics (mafic pyroclastics);
- 2 — metasandstones interbedded by keratophyre metapyroclastics;
- 3 — altered grey metasandstones with black phyllite intercalations;
- 4 — coarse laminated metasandstones intercalated by green-grey phyllites;
- 5 — ore veins;
- 6 — mining levels;
- 7 — prospecting hole;
- 8 — faults;
- 9 — sampling location. The age of volcano-sedimentary complex is Late Paleozoic. The inset shows the location of the Rožňava ore field (ROF).

The raw samples were crushed, homogenized and quartered (Figure 1c), and then crushed again and sieved into several fractions, from below 0.1 mm to above 1 mm (see scheme in Figure 3). After that, both gravity separation and ElectroMagnetic Separation (EMS) were used for concentrating the tetrahedrite in the samples of the different fractions (Figure 4).

Without going into the experimental details, the conclusion was that EMS (dry way), was effective in significantly increasing the tetrahedrite concentration (approximately

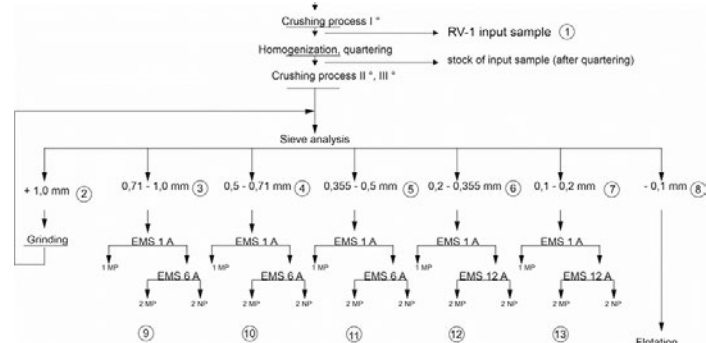


Figure 3 - Scheme of the raw mineral sample processing

80-97 wt%). Additionally, fractions below 0.5 mm show only minor differences in mineralogical composition with the presence of a small amount of accessory minerals.

Thus, on the basis of obtained results all the above-mentioned size fractions of raw sample will be merged and subjected to EMS (dry way) with the aim of obtaining approximately 10 kg of tetrahedrite product that will be used by our project partners to produce the mineral-derived sulphide p-type thermoelectric materials.



Figure 4 - Example of obtained concentrate after the EMS process: sample RV-13.

NEWS FROM WORK PACKAGE 3 “MATERIALS MODELLING AND PROCESSING”: ACTIVITY ON MECHANOCHEMICAL SYNTHESIS AND PULSE PLASMA COMPACTION OF TETRAHEDRITES

We will report here on Work Package 3 (WP3), which is dedicated to Materials modelling and Processing. In these first months, the WP3 activities have proceeded along several interconnected paths: (1) experimental modelling (Taguchi method) for the selection of optimum material composition (in terms of transition metal dopants in the tetrahedrite structure) to achieve the best TE efficiency, (2) process optimization for the production of tetrahedrites via mechanochemical synthesis (MCS), (3) optimization of the pulse plasma compaction (PPC) sintering conditions.

Measurements of Seebeck coefficient (S), electrical (α) and thermal conductivity (κ) have been performed on the first sintered samples, to determine the maximum efficiency, expressed by the dimensionless figure of merit, zT , according to the following equation:

$$zT = TS^2 \frac{\alpha}{\kappa}$$

Tetrahedrite-tennantite minerals are p-type thermoelectric materials characterized by very high values of S and extremely low values of κ , the latter is due to their complex unit cells (Figure 5a) and in particular to the out-of-plane vibrational mode of the Cu atom in the $\text{Sb}[\text{CuS}_3]\text{Sb}$ sub-unit shown in Figure 1c, which gives rise to strong phonon-phonon scattering, similarly to other poor thermal conductors such as skutterudites and clathrates².

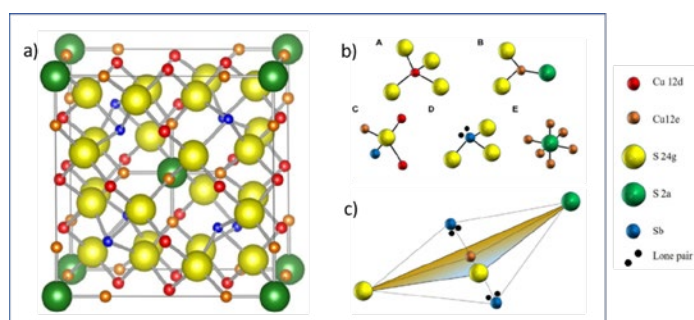


Figure 5 - (a) tetrahedrite unit cell, (b) coordination sub-units, (c) $\text{Sb}[\text{CuS}_3]\text{Sb}$ trigonal bipyramidal sub-unit, much likely related to the poor thermal conductivity of tetrahedrites. Reproduced from ref. 2.

Of general formula $\text{Cu}_{10}(\text{TM})_2(\text{Sb,As})_4\text{S}_{13}$, with TM being transition metals, the tetrahedrite-tennantite crystal structure offers huge potential for compositional variations. Common TMs present in natural mineral tetrahedrites are Fe and Zn, and in lower amounts Pb, Hg, Cd, Mn and others. Synthetic tetrahedrites can be successfully produced with many more different compositions, and zT values ranging from 0.6 for undoped tetrahedrite (TM = Cu), to values higher than 1 for specific combination of dopants have been reported². The nature and ratio of TMs has a considerable influence on the zT value, that is why the START project (and WP3, in particular) aims at selecting the most efficient composition of dopants and subsequently at producing the tetrahedrite with desired composition from a mixture of mineral and synthetic starting materials, using the highest possible amount of natural tetrahedrite from mine waste.

In these first months of work, we have selected two compositions, reported to have high TE efficiency³, and have optimized the synthesis parameters of MCS (Figure 6), obtaining monophasic doped tetrahedrites as fine powder materials. Several PPC sintering trials have been performed on the powder tetrahedrites, and the first measures of zT have already given promising values.

Meanwhile, material modelling is ongoing, the Taguchi method is being employed as an experimental modelling tool for researching other dopant compositions, with the aim of identifying compositions with even higher TE efficiency.



Figure 6 - Mixing of the powder elements for mechanochemical synthesis (left). MCS reactor facility at MBN (center) and sintered pellets by GeniCore (right).

The next steps of WP3 will focus on the mechanochemical synthesis of natural/synthetic tetrahedrites (maximizing the amount of mineral from mine waste). The composition of each mineral sample will be accurately analyzed and later adjusted by addition of the elements required to target the desired composition. On these powder materials, the optimized PPC sintering protocol will be applied and zT at different temperatures will be evaluated, from the measurements of α , κ and S .

START'S SCIENTIFIC ADVISORY BOARD APPOINTED

In November 2022, the START project consortium revealed the members of its Scientific Advisory Board (SAB). It is an external consulting body, appointed by the consortium's Executive Committee, consisting of experts from public/private organizations representing the scientific community involved in the project topics. According to Horizon Europe's requirements, it is strongly recommended that consortia involve their stakeholders as soon as possible in such a consulting body. The SAB members will provide constructive input and guidance on the project activities in order to maximize the visibility of the outputs and to achieve the project goals. Their opinions, although not binding for the consortium, will be highly considered by the consortium management.

We selected 3 external experts. In alphabetical order: Doug Crane, Jean-yves Escabasse, and Julie Hollis. They represent different stakeholders' sectors, from the minerals side to the thermoelectric industry, including R&D&I. We look forward to working with them in the next years and will introduce them to you one by one in this newsletter. In this issue, meet Julie Hollis (see in the relevant chapter)!



Figure 7 - The three members of START's Scientific Advisory Board. From left to right: Doug Crane, Jean-yves Escabasse, and Julie Hollis.

NEW EQUIPMENT ACQUIRED BY LNEG TO WORK ON START MATERIALS

In the framework of the project START, the following equipment were acquired by LNEG and are now in full operation:

- Vibratory Disc Mill “RS 200” and High Energy Ball Mill “Emax”. The RS 200, which allows very short grinding times with excellent reproducibility, is being used for crushing mineral samples in WP2 activities. On the other hand, the Emax is being used to process the p-type and n-type thermoelectric materials in WP3. The Emax combines high frequency impact, intensive friction, controlled circular jar movements and an innovative integrated water-cooling system that allows a substantial reduction in the processing time for mechanical alloying as well as a better transformation rate when compared to conventional ball mills.



Figure 8 - Retsch RS200 Vibratory Disc Mill.

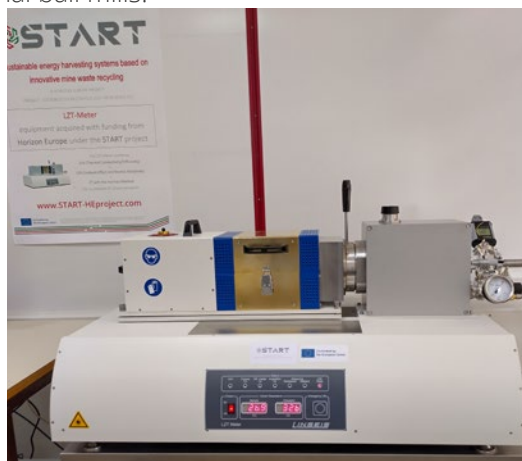


Figure 9 - Retsch Emax High Energy Ball Mill.



Figure 10 - Linseis LZT-Meter.

START WEBINARS

Among dissemination activities, we are organising a series of free webinars. Have you taken part in our first events?

The first START webinar took place on 28th February, 14:30-15:30 CET. It was dedicated first of all to an overview about the project, given by our coordinator F. Neves, of LNEG, and then to a presentation by D. de Oliveira, also of LNEG, that covered the issue of collecting mineral samples in a uniform way from the mines. All that was followed by a question time. We had more than 60 participants and the full recording of the sessions is freely available on our website and on our YouTube channel: if you want to rewatch it, follow this link: <https://youtu.be/kbLFV0B05aA>



Figure 11 - Advertisement of the 1st START webinar, held on 28th February 2023.

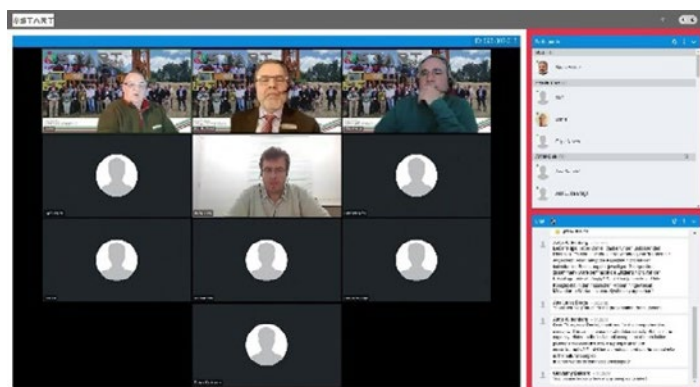


Figure 12 - Screenshot taken during the 1st START webinar on 28th February 2023.

The second START webinar was focused on Latin America, and took place on 26th April, 16:00-17:15 CEST. After a quick introduction by our coordinator, we had two speakers from important stakeholders in the area:

- Fredy Guzmán Martínez, head of Environmental Projects on the Servicio Geológico Mexicano (Mexican Geological Survey) and chief of the Mining Environmental Liabilities Expert Group of the Association of Iberoamerican Geological and Mining Surveys (ASGMI), who spoke about “Critical raw materials in mining environmental liabilities: A review”.
- Rafael Bittencourt Lima, geological researcher at CPRM - Serviço Geológico do Brasil (Brazilian Geological Survey) who addressed the topic “Tetrahedrite as an accessory mineral in Brazilian mineral deposits”.

At the end of the presentations, a few minutes of questions and answers closed the session. Participants were this time 30, including several interested attendees from a few American countries. Also this webinar is available for watching or rewatching here:

<https://youtu.be/m9hS7NNJOTw>.



Figure 13 - Advertisement of F. Guzmán Martínez (SGM) as speaker in the 2nd START webinar on 26th April 2023.



Figure 14 - Advertisement of R. Bittencourt Lima (SGB) as speaker in the 2nd START webinar on 26th April 2023.

A third event is scheduled, for the afternoon of 31st May, again at 14:30 CEST, and it will include presentations from European partners and experts, still related to the mining and minerals aspects of the project. A detailed agenda will be made public soon and registration for the event will be consequently opened. Stay tuned on our website and social media!



Figure 15 - Screenshot taken during the 2nd START webinar on 26th April 2023.

START AND GENDER BALANCE



Figure 16 - Three female members of the consortium were chosen to promote gender equality on the International Women Day.

In occasion of the International Women's Day, 8th March 2023, we wanted to show that we care. We had just completed an internal review of the gender balance in our consortium, that showed some good data and yet, as more generally usual in the whole society, with room for improvement: in fact, 40% of the people involved in START are women, with 1 female Work Package leader, 5 task leaders, and 3 team leaders.

On that date, we published contributions from three of our female colleagues. One is the CV of Patricia Almeida Carvalho of SINTEF, who is leading the Workpackage 4 "Materials Characterization" in the project; and then 2 videos, one from Gracia Olivenza (ASGMI, Spain) and the other from Concepción Fernández Leyva (IGME-CSIC, Spain), both giving insight in the project and on their role in the activities. You can find all details on our website: <https://www.start-heproject.com/1350-2/>

START ON THE MAGAZINE "POWDER METALLURGY REVIEW"

An article written by our team (with contributions from F. Neves (LNEG), B. Vicenzi (EPMA), A. Bianchin (MBN Nanomaterialia), M. Rosinski (GeniCore) and H. Yin (TEGnology)) was published on the Spring 2023 issue (vol. 12, n.1) of the well-known powder metallurgical magazine Powder Metallurgy Review. On page 89, the paper titled "The START project: Creating a sustainable supply chain for green energy harvesting products by Powder Metallurgy" includes an overview of START's motivation, approach, goals and expected impact, and, targeting the magazine's usual audience within the powder metallurgy community, more details into the powder metallurgy side of the project: how to derive powders from the tetrahedrite containing minerals and pure elements (by Mechanochemical Synthesis), and how to consolidate them (by Pulse Plasma Compaction) into functional materials and devices with good thermoelectric properties. Some initial data and images coming from the ongoing tasks are shown.

The full issue is freely available for reading and downloading in pdf version on the Powder Metallurgy Review website:

<https://www.pm-review.com/powder-metallurgy-review-archive/powder-metallurgy-review-spring-2023-vol-12-no-1/>

We thank Powder Metallurgy Review and Inovar Communications Ltd for the attention given to our project!

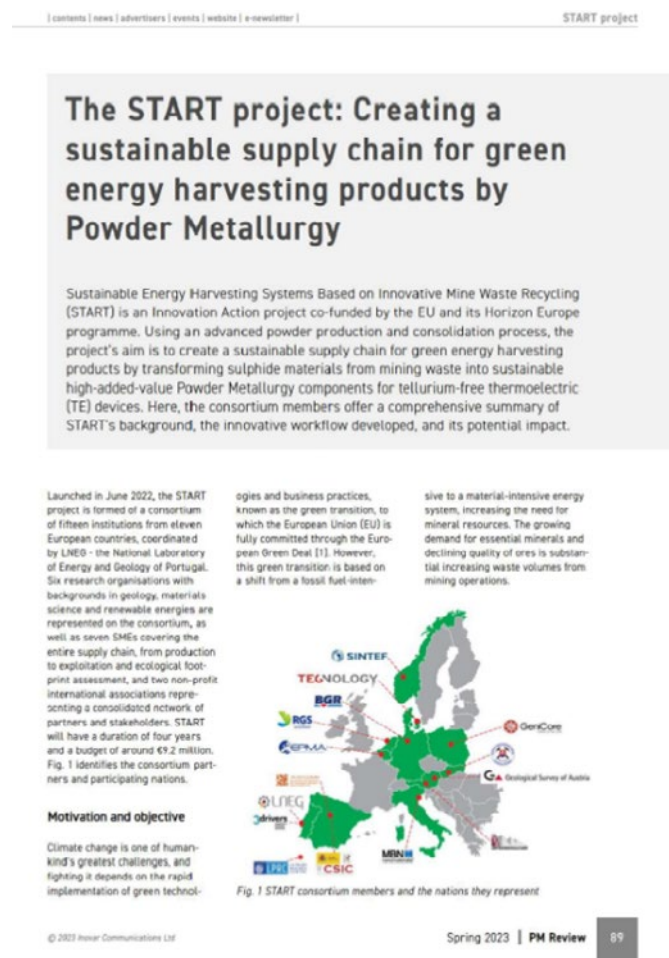


Figure 17 - The first page of our article in the Spring 2023 issue of Powder Metallurgy Review.

START ON THE MAGAZINE "ÁGUA&AMBIENTE"

A Portuguese magazine dealing with the environment (energy, waste and water issues), “água & ambiente”, a magazine with about 1200 printed copies, hosted an article (in Portuguese) about our project in its November-December 2022 issue⁴. The original title was “Projeto START vai transformar resíduos de minas em produtos para dispositivos termoeletrônicos” (“The START project will transform mine wastes into thermoelectric devices”). It is a detailed interview with our coordinator F. Neves (LNEG) that fills page 48 and 49 of the magazine.



Figure 18 - The START project featuring on “agua & ambiente” Nov-Dec 2022, pages 48-49.

START ON THE MAGAZINE "INGENIUM"

The magazine "Ingenium" published by the Ordem dos Engenheiros (the Portuguese Professional Association of Engineers), that is distributed to all members of that association (around 60000) hosted a short info, in Portuguese, about the project in its April-May-June 2023 issue n. 180, page 114⁵. The main features of START were summarized and a link to our website was given.



Figure 19 - The news about START in *Ingenium*, n.180, p.114.

STARTY IN 12 LANGUAGES!

You already know Starty, that is usually the front “man” of our communication. To make Starty more widely understandable, we made the effort of covering a large part of the EU official languages, and even more. We have made our comics author J. Mascarenhas (LNEG) work hard to deliver new versions of his comic strip involving the robot Starty in twelve different languages! He received the contribution from many of our consortium partners, with the translation of the original Starty strip (that you have seen in Issue 1 of our newsletter) into their mother tongues. All in all, we have collected in the document that you can download from this link or from the Documents page the following languages: Danish, German, English, Spanish, French, Italian, Dutch, Norwegian, Polish, Portuguese, Slovakian, Turkish.

You can find the multilingual edition of “Starty explains START” on our website’s Documents page!



Figure 20 - Starty loves all languages!

START DISSEMINATION EVENTS

In the second part of the first year, START continued to take part in events with some of its consortium members.

PDAC 2023, The World’s Premier Mineral Exploration & Mining Convention, Toronto (Canada), 5th-8th March 2023

The project START was present at the PDAC (Prospectors and Developers Association of Canada) 2023 edition, which took place in the Toronto Convention Centre from 5th to 8th March. The event attracted almost 24000 attendees from 133 countries, 2500 investors, and hosted 1050 exhibitors.



Figure 21 - Delegates during a session at PDAC 2023 (from PDAC’s website).



Figure 22 - Exhibition at PDAC 2023 (from PDAC’s website).

A continuous presentation outlining the projects objectives and goals was shown during the event in the EU booth. This presentation generated interest amongst visitors to the booth.



Figure 23 - Left: Presentation about START on show at the PDAC 2023; right: the EU booth that hosted START.

ASGMI General Assembly Santo Domingo (Dominican Republic), 17th-21st April

ASGMI held its General Assembly from April 17th to 21st in Santo Domingo (Dominican Republic).



Figure 24 - Delegates at the ASGMI General Assembly 2023.



Figure 25 - G. Olivenza (ASGMI) at the ASGMI General Assembly 2023.

During the Assembly, a workshop was held on “The role of geological services in the ecological and energy transition,” and there were talks from the different participating geological services on the state of the art in the identification and characterization of critical minerals in their respective countries, among other topics.

The Vice President of the Government, Raquel Peña, and the Minister of Energy and Mines of the Dominican Republic attended the opening ceremony. Also, the Minister of Mining of Guatemala and representatives from international institutions that are not part of ASGMI, such as UNEP and USGS, joined the event.

During the talks, the activity report of ASGMI's expert groups was presented, specifically the groups on mining environmental liabilities and mineral resources participating in the START project. The project was discussed, the presentation video was shared, and the next webinar, the second START free webinar, which was held the following week, was announced.

International Conference “Sourcing the European energy transition from domestic resources – vision or wishful thinking”, Uppsala (Sweden), 25-26th April 2023

START was present also in this conference, hosted by the EU HORIZON 2020 project GREENPEG, in cooperation with the Swedish Association of Mines, Minerals and Metal Producers (SVEMIN) and the European Technology Platform on Sustainable Mineral Resources (ETP SMR) in Uppsala, in 25th-26th April. Some informative material and a rollup about the project were exhibited.



Figure 26 - The START rollup shown at the conference organised in Uppsala by the GREENPEG project.

Around 100 participants from all around the globe were attending the conference. Part of the conference was about topics regarding the EU's Green deal and how the actual geopolitical situation is affecting global supply chains. The START project attracted the interest of attendees based on the fact that waste material like domestically sourced tetrahedrite could fill gaps in those supply chains.

GREENPEG invited the START consortium to give more detailed information in the form of a webinar in the near future.

EPMA General Assembly 2023, Brussels and hybrid, 27th April 2023 – and other events



During the General Assembly of the European Powder Metallurgy Association (EPMA), F. Neves (LNEG) gave a thorough presentation of about 30' to present the project in detail, with a focus on the powder metallurgy content in the project, to address the interests of the audience, about 30 people consisting of members of the association and a few invited speakers. The event was held in a hybrid format on 27th April 2023, with some participants in Brussels (legal address of the EPMA), and some connected remotely. In addition to that, in the morning B. Vicenzi (EPMA) had showed in a slide the main features of the project whilst reviewing the activity of the association in EU funded projects.

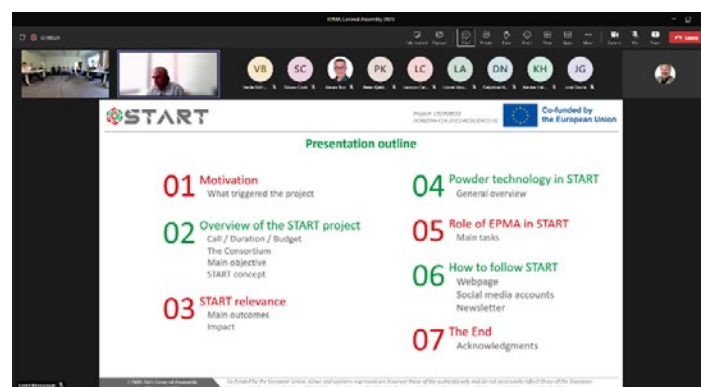


Figure 27 - Screenshot taken during F. Neves presentation of the project in the EPMA General Assembly 2023.

Additionally, the two technical managers of EPMA have given information about the activities of START during the seminars held in early 2023, namely the Hot Isostatic Pressing seminar in Dresden (8th-9th March) and the Press&Sinter seminar in Barcelona (28th-29th March). In the latter occasion, some promotional materials about START (leaflet and the issue of Powder Metallurgy Review containing the article on the project) was also available to the about 25 delegates.



Figure 28 - Among the literature available for the EPMA seminar “Progress and Challenges in Press&Sinter” there was also the START flyer.

Future events

START is currently deciding which events to attend in the next months. For the moment we are thinking of:

- A training lecture on “Thermoelectric Materials and the START Project” is foreseen at the EPMA Powder Metallurgy Summer School that will take place in Dresden, at the Fraunhofer IFAM, from 17th to 21st July 2023
- A booth will be again prepared at the EPMA Euro PM2023 Congress & Exhibition that will be held in Lisbon, from 1st to 4th October 2023
- Plus, numerous other smaller events where project partners will bring information and short presentations about the project.

We will also repeat the participation in most or all of the events already covered in 2022. So maybe you will meet us in some of these events! Do not hesitate to get in touch directly!

TECHNICAL PILLS

TETRAHEDRITES IN THE WORLD

Tetrahedrite-(Zn) is a copper antimony sulfosalt mineral from the so called Tetrahedrite Group including Tetrahedrite, Tennantite, and Freibergite. Tetrahedrite with the formula $\text{Cu}_6(\text{Cu}_4\text{Zn}_2)\text{Sb}_4\text{S}_{13}$ is the antimony end member of the continuous solid solution series with arsenic-bearing tennantite and the silver-rich variety Freibergite.

Mineral

The name of the mineral derives from its tetrahedron shaped cubic crystals with a density of 4.97 g/cm^3 . The colour of the mineral is steel grey to black metallic and a Mohs hardness of 3.5 – 4, comparable with Fluorite.



Figure 29 - Tetrahedrite Subgroup mineral from Georg Mine, Germany. Source: mindat.org

Tetrahedrite like other sulfosalts is an economic copper ore with an average copper content of 34.8 %. The silver rich Freibergite has a silver content up to 18 % and it was an important silver ore in the area of Freiberg in Saxony, Germany.

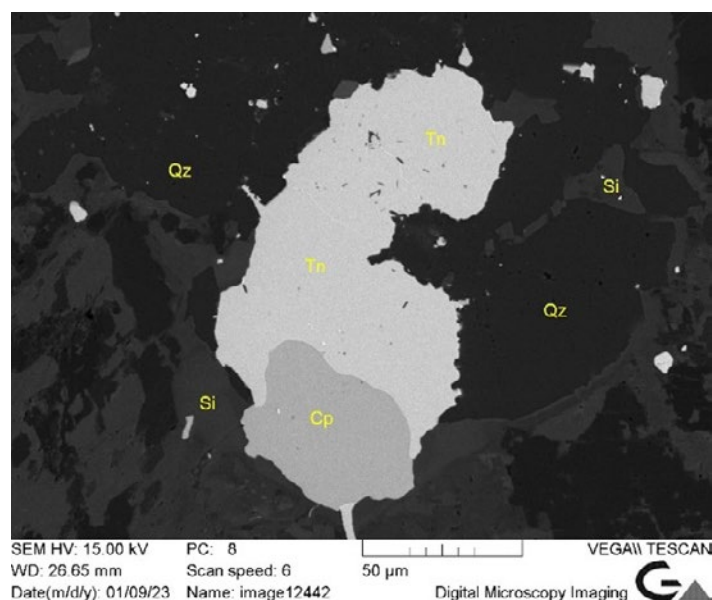


Figure 30 - Microscopy of an ore from Leogang, Austria. Qz: Quartz, Si: Siderite, Cp: Calcopryrite, Tn: Tennantite

Occurrences

Tetrahedrite occurs in low to moderate temperature hydrothermal veins and in some contact metamorphic deposits, associated with Arsenopyrite, Baryte, Bornite, Calcite, Dolomite, Fluorite, Galenite, Pyrite, Quartz, Siderite, and Sphalerite. Around 6000 occurrences around the world are documented.

Occurrences in Germany have been reported in Baden-Württemberg (e.g. near Freudenstadt), in Saxony (e.g. Erzgebirge), and in other places from Rhineland-Palatinate to e.g. North Rhine-Westphalia, Lower Saxony, and Saxony-Anhalt. In Austria, Kärnten, Salzburg Land, Steiermark and the area of Brixlegg in Tirol are the main places where Tetrahedrite occur and had been mined since Celtic times.

In Switzerland it is known from occurrences from Val d'Anniviers and Graubünden. The occurrence in the French Pyrenees is famous for their huge crystal size up to 25 cm. The famous Herodsfoot Mine of Lanreath, Liskeard District, Cornwall, England, has produced excellent crystals of this mineral, almost always associated with golden Chalcopyrite.

Peru has produced the finest Tetrahedrite crystals in a wide range of different localities, e.g., Casapalca or Mundo Nuevo Mine. Another important South American locality is the Machacamamarca District in Bolivia. Bingham Canyon is an important locality in the US.



Figure 31 - Localities for Tetrahedrite (numbers), mining sites (mallet and iron). For more details and a full legenda of symbols, refer to <https://www.mindat.org/min-3924.html>

POWDER METALLURGY OF TETRAHEDRITES

Powder technology is one of the processing technologies that are being used to produce mineral-derived p-type thermoelements. The approach followed in the START project is schematically summarized in Figure 32 and includes three main steps:

- 1) Direct synthesis of nanostructured powders of the mineral-derived p-type material by mechanochemical synthesis (MCS).
- 2) Consolidation of the powders produced in step 1 by pulse plasma compaction (PPC) to produce bulk materials.
- 3) Assembly and production of the TE devices incorporating the mineral-derived p-type thermoelements produced in step 2.



Figure 32 - The use of powder technology in START and main partners involved in this activity.

MCS, a solid-state synthesis route using high-energy ball mills and already in use for large-scale production by MBN⁶, is a suitable and fast way to produce sulphide semiconductor powders^{7,8}. During the MCS process, the chemical reactivity is promoted under non-equilibrium conditions, near room temperature, by unbalanced mechanical forces with the transfer of the mechanical energy to the powder particles resulting in the introduction of strain into the powder, through the generation of dislocations and other defects that act as fast diffusion paths changing the reactivity of the powders⁸. Moreover, mechanical deformation occurs on a local basis, being mediated by dislocations and other lattice defects. As a result, the mass transport process will be reduced relative to that of high-temperature solid-state diffusion, with a great impact on the chemical and physical behaviour of the compounds. There are several variables which influence the MCS process, e.g., type of the mill, material of milling media, ball-to-powder ratio, filling extent of the milling chamber, milling atmosphere, milling speed, milling time, etc.⁸.

PPC is a modification of the conventional spark plasma sintering (SPS) process⁹. In PPC, the energy stored in a capacitor bank and charged to several kV, is delivered to the powder in short pulses of hundreds of μ s with a frequency up to 200 Hz, using the oscillating capacitor discharge to produce current surges with an amplitude of the first half-wave of several tens of kA. The high voltage and short pulses result in power values up to 80 MW and field-enhanced diffusivity enables full densification at lower temperature setpoints than in conventional SPS, where low-voltage electric fields are employed¹⁰. SPS-based technologies have proven to be a viable consolidation technique for sulphide-based powders to achieve a full-density compaction at temperatures considerably lower than the melting point allowing the nanostructures developed by the MCS process to be retained. Other advantages of SPS include fast-heating rate, short cycle time, accurate control of sintering energy, high reproducibility, safety and reliability.

The use in the START project of the innovative PPC device, and of the upgraded field assisted sintering technology (U-FAST), both developed by GeniCore, is expected to result in more appropriate densities and materials stability improvements preventing thermally induced solid-state reactions in the TE material during service, which will be beneficial for the overall TE performance. The production of square samples in place of the traditional cylindrical compacts will be assessed. From a technological point of view, this will represent a cost-effective solution and a huge step forward in the consolidation of parallelepiped thermoelements required for device assembly for large-scale applications.

Sulphur-based compounds are a vast class of materials, some of which are semiconductor materials with exceptional properties for energy conversion applications, either as thermoelectric materials or as photovoltaic materials^{7,11,12,13}. Among these, the tetrahedrite-tennantite series has the great advantage of being naturally occurring and often considered as waste by the mineral processing industries, as mentioned above.

Unfortunately, the thermoelectric properties of natural tetrahedrite-tennantite, and its thermal stability, are not good enough for commercial exploitation, because of the presence of other phases (i.e., famatinite) and other minerals (e.g., pyrite, chalcopyrite, and quartz). The refinement of pure tetrahedrite-tennantite by conventional mining processes is not economically viable, but its direct use as raw material in the production of modified tetrahedrite-tennantite by powder technology processes is a promising route.

Tetrahedrite-tennantite powders can be obtained by solid-state processing route from the elements, with relatively small effort, but a more cost-efficient approach is to start from minerals with known composition and balance it with elemental powders. With this approach, minerals coming from different sites, hence with different compositions and structures, can be processed with a dedicated material balance, targeting the same thermoelectric performance.

At the laboratory level, the effectiveness of processing natural and synthetic tetrahedrites has been already demonstrated in the range of grams⁷, and it is now scaled by a factor of x100, approaching a relevant pilot scale production.

With the support of the Lundin Mining Company, tetrahedrite-tennantite mineral from the Neves-Corvo mine (Portuguese zone of the Iberian Pyrite Belt) has been used, and it has been processed with 20%, 50% and 80% of synthetic tetrahedrite (Figure 33), testing two different processing routes. Both routes are based on industrial MCS apparatus using plants designed by MBN nanomaterialia spa¹⁴, which favours a direct transfer of impact energy to the processed material. The milling chamber is cooled to work near ambient temperature and the process is done in Argon atmosphere.

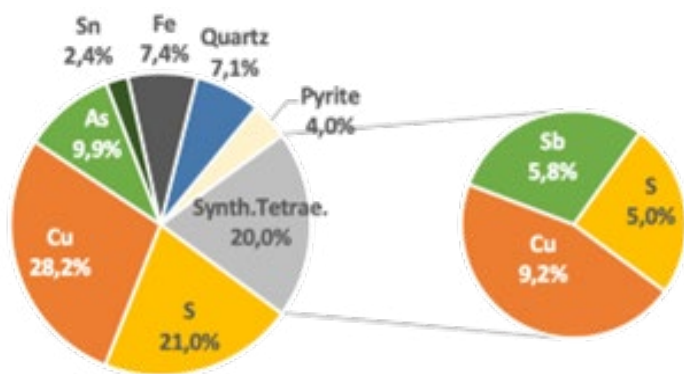


Figure 33 - Composition of the processed powder mixture with 20% of synthetic tetrahedrite.

The first route is more conservative; the synthetic tetrahedrite is formed previously in a different MCS process and then added to the natural mineral for the final mixing. The second route consists in a direct MCS of the natural mineral with the elemental copper, antimony and sulphur powders, balanced as in the first route for consistent benchmarking. This second route is more challenging but provides more flexibility when the attempt is more about alloying new elements into the tetrahedrite-tennantite rather than dispersing synthetic tetrahedrite into the natural-occurring one.

The backscattered electron images from Figure 34 do not reveal substantial differences between the material obtained in the two routes, not even at lower magnification as regards pyrite (dark grey) and quartz (darker spots) distribution.

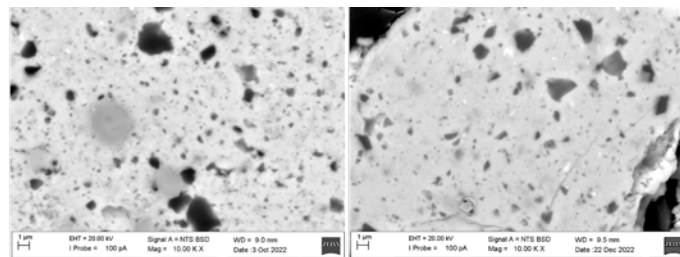


Figure 34 - Typical backscattered electron images of the processed materials when starting from powder mixtures of: left image - mineral/synthetic tetrahedrite (first route), right image - mineral/elemental powders (second route).

Typical X-ray diffraction (XRD) patterns for some of the processed materials are shown in Figure 35. The XRD patterns confirm that the two routes are consistent with each other; a small difference appears in the famatinite peak, which is promoted when processed directly from powders mixtures containing elemental powders. This is a positive result since it confirms that the two routes are equally effective, and it opens the way for the direct processing via MCS of natural tetrahedrite-tennantite material with metals and sulphur powders for the production of thermoelectric materials.

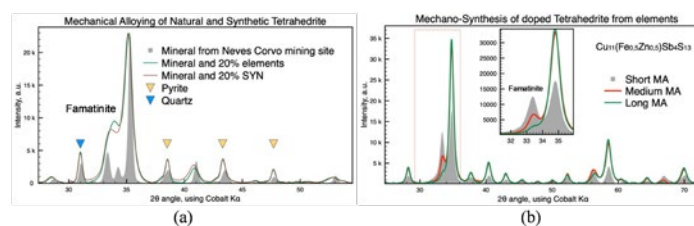


Figure 35 - (a) Typical XRD patterns of the mineral and some of the processed materials. (b) Typical XRD patterns for doped synthetic tetrahedrite as function of the MCS energy level.

The formation of famatinite, which is an unwanted phase, is due to the lack of stabilizing elements such as Fe and Zn as substitutes of Cu in the synthetic tetrahedrite utilized in the experiment. In fact, the synthesis of doped tetrahedrite reduces the formation of famatinite when higher MCS energy levels are used (Figure 35). This synthesis has been done in industrial plants to validate the feasibility of the approach. The next development steps are therefore related to the identification of the most effective combination of substitutional elements that will be used as a reference target in the processing of minerals with metals and sulphur powder.

This approach will enable the enhancement of naturally occurring tetrahedrite-tennantite to make it an effective thermoelectric material and has the potential to be transferred to other combinations of minerals and metals for the synthesis of functional materials.

MEET THE SCIENTIFIC ADVISORY BOARD MEMBERS

In the next issues, we will present you the members of our Scientific Advisory Board. We will do that by means of short interviews where they will highlight their activity and the activity of their institutions and companies. We start with Julie Hollis, Secretary General of the EuroGeoSurveys.

Julie HOLLIS (EuroGeoSurveys)



Figure 36 - Julie Hollis is Secretary General of EuroGeoSurveys (EGS) – The Geological Surveys of Europe – a geoscience liaison point with the European Commission, EU institutions, and other stakeholders including academia, industry, and professional associations. Her focus is steering EGS toward becoming a sustainable Geological Service for Europe, supporting the EU's green energy and digital transition. Previously, Julie led the Department of Geology for the Ministry of Mineral Resources in Nuuk, Greenland, and has also worked for 3 geological survey organizations in Australia and Denmark, managing regional geoscience mapping programs. Julie has a BSc from the University of Sydney, and PhD in Geology and Master of Science Communication and Public Engagement from the University of Edinburgh

What are the mission and objectives of the EuroGeoSurveys (EGS) and how do you work to accomplish them?

EuroGeoSurveys is a not-for-profit organisation representing 37 Geological Surveys of Europe. We provide the European Institutions, regulators, industry, and the public, with expert, balanced and practical pan-European geoscience data and advice to guide policy and to address key societal challenges, supporting the EU's competitiveness, social well-being, environmental management and international commitments.

We do this by coordinating the network of the Geological Surveys of Europe and through the collaborative research and activities of our Expert Groups and Task Forces. Through our European Geological Data Infrastructure (Figure 38), we provide open-access, harmonised geological maps, and data to inform EU, local and national policy, and for the benefit of all European citizens.

Our vision is to establish a unified Geological Service for Europe based on a common European Geological Knowledge Base.



Figure 37 - Excerpts from the EGS website.

How is EGS contributing to the EU priorities related with the application of the European Green Deal and the EU Action Plan on Critical Raw Materials?

At the heart of the collaboration between the Geological Surveys of Europe is our ambition to establish a sustainable Geological Service for Europe, serving European society through, and beyond, the green transition.

Through a five-year Coordination and Support Action, the Geological Service for Europe project (GSEU), EuroGeoSurveys will deliver a plan for a sustainable Geological Service for Europe to be implemented beyond the 2027 project end. This service will serve European society and inform sound policy in water, energy, raw materials, hazards, and all areas that require subsurface data and expertise. Through this service, we will contribute to environmental sustainability and social well-being in Europe, supported by a powerful and comprehensive digital infrastructure and a strong network of geoscience experts.

EuroGeoSurveys and our member Geological Surveys of Europe play a key role in the EU Action Plan on Critical Raw Materials. EGS has a long history of collaborative research (e.g., ProMine, Minerals4EU, euRare, SCRREEN, and GeoERA, including the FRAME project) and science for policy advice regarding CRMs. This is continued, compiled, and expanded within GSEU project.



Figure 38 - European Geological Data Infrastructure (EGDI) website: map of all Critical Raw Materials resources occurrences in Europe¹⁵.

What strategies can be adopted to improve the sustainability of Europe's raw material value chains, and in particular to fuel the European energy transition with domestic resources?

There is much to be done to build EU resilience in regard to CRM security. A comprehensive framework for supporting the whole CRM value chain has recently been outlined in the proposed CRM Act. Developing domestic supply is a crucial component of the required work and both primary and secondary resources will be important. Our work currently underway within the Geological Service for Europe Project builds on many previous projects and expertise gained to provide services and knowledge to increase sourcing of primary and secondary CRMs in Europe and decrease import dependency. This includes establishment of an International Centre of Excellence on Sustainable Resource Management supported by UNFC and UNRMS expertise, an atlas of primary and secondary CRM resources in Europe, including potential and favourability maps. The expertise of the European Geological Surveys is recognised in the proposed CRM Act, which mandates the national surveys to carry out national programmes of geological data acquisition, processing, and delivery to promote CRM exploration investment in Europe. This data and knowledge acquisition and delivery will be a key driver in the discovery and development of future CRM resources in Europe.

What is the position of the EGS concerning the Horizon Europe Framework Programme for Research and Innovation?

EGS recognises the importance of the EU Framework Programmes for Research and Innovation in developing excellent research and fostering pan-European as well as international collaboration activities in support of the European Research Area. EGS has a long history of engagement in the Framework Programmes, mainly through the collaboration of its members and Expert Groups and more recently with the involvement of the organisation itself in a number of key strategic projects aimed at pooling the expertise and knowledge available within the national Geological Surveys in support of EU policy priorities, namely through the GeoERA ERA-Net programme, addressing the themes of geoenery, groundwater, raw materials, and an information platform, and now the GSEU project. The Framework Programmes not only offer the opportunity to collaborate across borders, but also the ability to cluster with other relevant and complimentary research projects and reach out to stakeholder communities not always available at national level, boosting the potential impact of the research being undertaken. This has been important for EGS in growing our network and opening relations with new partners.

What is the aspect of the START project that you find more appealing, and why?

The START project is an excellent example of research and innovation that covers the full spectrum from basic to applied research through to pilot implementation and scaling up, in the process also building expert networks across public and private sectors, government, academia and industry. From an EGS perspective, our CRM experts are largely focussed on the upstream end of the value chain and while we aim to support sound science-based decision making that will have positive impact at the downstream end, we rely on our stakeholders and partners to have a greater engagement at this other end of the spectrum. START provides a valuable opportunity for building these networks and for identifying and addressing roadblocks through collaborative cross-sectoral research and innovation efforts.

Where do you see the best chances of synergies between EGS and START?

EGS has a wealth of data and expertise on European primary and secondary CRM resources and potential. A key point of intersection between EGS and START will be in linking the findings of START in relation to the most suitable mine wastes for the thermoelectric technology with the EGS expertise on Europe's secondary mineral resources. These secondary mineral resources are a focus of the current GSEU project and will be an area of increasing focus for the Geological Surveys of Europe as they plan for providing data and knowledge needed to implement the future CRM Act.

Thanks Julie!

CONSORTIUM TOUR

We continue our tour of consortium members: in this issue, two industrial partners that are already active in the thermoelectric device market. Meet TEGnology (Denmark) and RGS (the Netherlands).

TEGNOLOGY

TEGNOLOGY

TEGnology ApS is one of START's industrial partners, who is specialized in developing thermoelectric generators (TEGs) with advanced thermoelectric materials and novel module design. As a DeepTech Danish startup company, we provide more sustainable and cost-efficient TEGs, and expand our business to customized self-powered IoT devices. TEGnology has substantiated its new design (World Patent: WO2023031269A1) of a flexible TEG module (Flex-TEG®) in 2022 and started production thereafter. The company's business is to develop and sell cost-efficient and endurance TEGs as well as providing consultancy services in this field. Its potential is to provide TEG components for self-powered IoT devices, which are in large demand for many application areas such as smart construction/buildings, industrial factories, power plants, private homes, etc. Our products have been sold to end users including Novo Nordisk, Alfa Laval, Novozymes, etc.



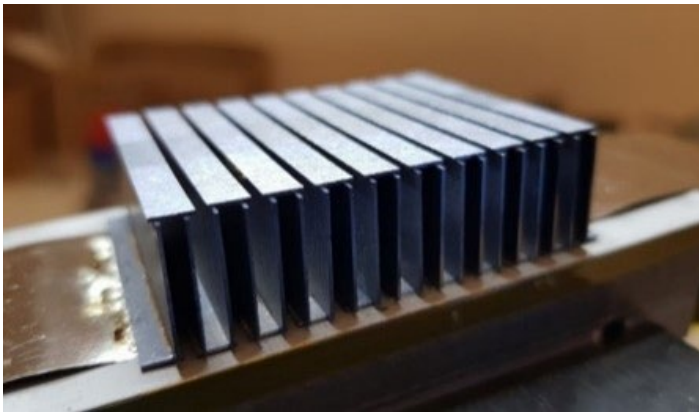
In the START project, TEGnology will use the expertise to demonstrate that the new mineral-derived tetrahedrite p-type thermoelement, can be fabricated in a production relevant environment and integrated with commercial TE devices with system design in a cost-efficient way. On the other hand, TEGnology will help to identify the suitable n-type thermoelectric materials for matching the p-type mineral-derived sulphides compositions.

www.tegnology.dk

RGS DEVELOPMENT

RGS Development is a technology company, promoting advanced silicon materials and devices for static power generation. Located in Broek op Langedijk (The Netherlands), a team of highly skilled employees are developing thermal electric materials and remote power solutions, supporting the global drive in the sustainable energy transition.

RGS development is founded by Energy Research Centre of the Netherlands (ECN) in 2000 initially to produce pSi wafers for Solar PV. Since 2013 the company has expended their activities around the application of Silicon in power generation and storage. Under the brand name Thermagy it operates the design and manufacturing of silicon germanium based thermoelectric materials and thermoelectric solutions. Under the brand name Solwafer it develops and manufacturers advanced silicon components for next generations of solar pv and thermophotovoltaics. Furthermore, it serves as technology provider for E-magy (www.e-magy.com), which introduces nano porous silicon for the next generation Li-ion batteries.



RGS development participates in a growing number of projects related to remote power generation in various industries such as Aerospace and Security and Combined Heat and Power generation (CHP). RGS provides expertise and knowledge on Silicon and the manufacturing of thermoelectric devices, for projects such as Integral, Sparc-ee, Wraps, and Next Gen RTG programs.



RGS development contributes in the START project a large expertise on the production of silicon-based materials (including TE materials, e.g., $\text{Si}_{1-x}\text{Ge}_x$) by a proprietary casting process technology (the Ribbon Growth on Substrate), and on designing and engineering TE devices for waste heat recovery systems and combined heat and power (CHP) systems. It will use its casting technology for producing the mineral-derived tetrahedrite p-type, in WP3, and will provide the n-type $\text{Si}_{1-x}\text{Ge}_x$. It will lead WP5 and will use its fully in house manufacturing capability for TE devices to adapt the ThermagyTM device to incorporate and validate the RGS-cast mineral-derived tetrahedrite p-type thermoelement. RGS will prepare for and anticipate on the integration of the TE devices into CHP and Waste Heat Recovery applications.

www.rgsdevelopment.nl

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CONTACTS

START regularly updates its website and social media with news about its activities, but also with more general documents and info on the topics of relevance for the project. Thermoelectricity, waste heat recovery, mine waste remining, sustainability, raw materials and critical raw materials, energy efficiency, and many others.

If you are interested in receiving this newsletter and other special news from the project directly in your mailbox, consider subscribing our mailing list on the website ("Contacts" page, "subscribe" section)! Clicking on the "Subscribe" button, you will fill a form generated by SendinBlue, our mailing system, and will subsequently receive an E-Mail to confirm your address. Your data will be treated and stored in accordance with the EU GDPR Regulation. And do not forget to follow all our social media accounts! Here is the list of the important links to click to reach our news:

Website: <https://www.start-heproject.com/>

Twitter: https://twitter.com/START_HEproject

LinkedIn: <https://www.linkedin.com/company/86266991/>

Twitch: https://www.twitch.tv/start_he_project

YouTube: <https://www.youtube.com/channel/UCHVjEhpVz9uaEgzlCj2lnPA>

SlideShare: <https://es.slideshare.net/StartProject/>

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